

Cuban coral traces annual hydrologically driven variability in $\delta^{234}\text{U}$ values since the end of the Little Ice Age

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15 **Abstract.** The natural uranium isotope ratio of $^{234}\text{U}/^{238}\text{U}$ in seawater behaves conservatively at basin scale, yet it can be regionally affected by continental freshwater discharge at decadal to centennial timescales. Here, we analyse annual variations in the $^{234}\text{U}/^{238}\text{U}$ isotope ratio, expressed as ‰-deviation from radioactive equilibrium as $\delta^{234}\text{U}$, of a coral from Cuba. Over the past 237 years, the mean $\delta^{234}\text{U}$ value of the coral was 145.7 ± 0.1 ‰ ($1 \sigma_M$), which is identical to that of modern open ocean seawater, whereas the average variation over the past century has been ± 3.7 ‰. This moderate variability is, however, 20 significantly greater than the external precision and reproducibility of measurements of ± 0.55 ‰ ($2 \sigma_M$). Moreover, the $\delta^{234}\text{U}$ values coincide inversely with regional precipitation, suggesting excess ^{234}U contribution from regional freshwater runoff. The most important finding is a strong increase in annual $\delta^{234}\text{U}$ variability to ± 8.1 ‰ during the end of the Little Ice Age (LIA, 1778–1847). We suggest that the increased $\delta^{234}\text{U}$ dynamics reflect substantial excess ^{234}U contributions from the Mississippi, far greater variability in the local freshwater fluxes to the Gulf of Mexico, and/or reduced advective currents during the LIA. 25 This study demonstrates that yet unexplored variability in coral $\delta^{234}\text{U}$ records within the presently known range of seawater $\delta^{234}\text{U}$ may be attributed to local and advected freshwater sources, which opens a new pathway for reconstructing these processes over time. Moreover, it places strong constraints on the initial $\delta^{234}\text{U}$ variability of fossil corals in light of ultra high-precision $^{230}\text{Th}/\text{U}$ dating.

1 Introduction

30 In the modern ocean, uranium is conservative, with a residence time of 200–400 ka (Ku et al., 1977; Dunk et al., 2002), far larger than the global ocean mixing timescale of approximately 1 ka, which allows for homogenization of the U content with

a conservative behaviour vs. salinity (Not et al., 2012) and isotopic composition of the world oceans. Consequently, owing to the continuous production of ^{234}U via ^{234}Th and ^{234}Pa from the decay of ^{238}U , with a half-life of 4.4683×10^9 years (Jaffey et al., 1971; Ivanovich & Harmon, 1992; Cheng et al., 2013), the activity ratio of $^{234}\text{U}/^{238}\text{U}$ (also expressed as ‰-deviation from radioactive equilibrium $\delta^{234}\text{U}$) in seawater also remains predominantly conservative (Henderson, 2002; Robinson et al., 2004a; Andersen et al., 2010).

However, seawater $\delta^{234}\text{U}$ ($\delta^{234}\text{U}_{\text{sw}}$) is in radioactive disequilibrium in the global ocean (Ku et al., 1977; Chen et al., 1986; Delanghe et al., 2002; Robinson et al., 2004a; Andersen et al., 2010; Andersen et al., 2015; Kipp et al., 2022) due to the continuous input of excess ^{234}U from rivers and submarine groundwater (Robinson et al., 2004a; Andersen et al., 2010; Li et al., 2023). Typically, these waters are enriched in ^{234}U due to the α -recoil process of radioactive decay from ^{238}U to ^{234}U , leading to preferential release of ^{234}U into the hydrological environment (Kigoshi, 1971; Chabaux et al., 2008). ^{234}U enrichment is highly variable (Dunk et al., 2002) and is influenced by physical and chemical weathering, resulting in the global ocean exhibiting an excess of approximately 15 ‰ from secular equilibrium (Ku et al., 1977; Chen et al., 1986; Delanghe et al., 2002; Robinson et al., 2004a; Andersen et al., 2010; Andersen et al., 2015; Kipp et al., 2022). A recent reassessment of the open ocean confirmed a constant $\delta^{234}\text{U}$ value of 145.55 ‰ (standard error of the mean (σ_{M}) = ± 0.28 ‰), with a range of 1.30 ‰ (Kipp et al., 2022). Modern corals have been analysed for their $\delta^{234}\text{U}$ values to confirm the $\delta^{234}\text{U}_{\text{sw}}$ uniformity observed in modern ocean far from continental sources of marine uranium (Chen et al., 1986; Delanghe et al., 2002; Robinson et al., 2004b; Andersen et al., 2010; Andersen et al., 2015; Kipp et al., 2022). Variations in the $\delta^{234}\text{U}$ values of fossil corals have been attributed to either diagenetic overprint or large-scale ice volume (climate)-driven changes in the excess ^{234}U flux (Dunk et al., 2002; Henderson, 2002; Robinson et al., 2004a; Robinson et al., 2004b; Esat & Yokoyama, 2010; Chutcharavan et al., 2018). Several studies have proposed that per mil deviations from modern ocean $\delta^{234}\text{U}$ values observed in fossil corals during the last glacial maximum reflect sea-level control on the excess ^{234}U flux (Esat & Yokoyama, 2006, 2010; Chutcharavan et al., 2018). The observed 4–8 ‰ decrease in glacial seawater $\delta^{234}\text{U}$ values is suspected to represent a reduction in continental runoff or the oxidation and release of U stored in interglacial deposits of U from the reducing environment of, for example, mangrove forests. A recent study further revealed elevated $\delta^{234}\text{U}$ in relation to an Antarctic meltwater plume (Li et al., 2023). Nevertheless, the reconstruction of past $\delta^{234}\text{U}$ values can be hampered by subaerial coral diagenesis (Scholz et al., 2004; Frank et al., 2006) or U-series open system behaviour caused by the recoil process of coral embedded sediment (Henderson et al., 1993; Gallup et al., 1994; Henderson & Slowey, 2000; Thompson et al., 2003; Villemant & Feuillet, 2003; Frank et al., 2006). Tropical surface-dwelling corals are always situated in shelf environments, with potential influences of U contributions from local river discharge, submarine groundwater releases, or even the distant transport of freshwater from larger river systems. Consequently, by examining postmodern, well-preserved and annually resolved corals, the oceanic U isotopic composition can be investigated to identify any potential systematic local or regional disturbances from freshwater fluxes through rivers and submarine groundwater. To detect subtle changes in oceanic and coral U isotopic compositions, multicollector inductively coupled plasma source mass spectrometry (MC-ICP-MS) is a well-established precise instrumentation for isotopes, that offers external reproducibility better than 1 ‰. Thus, we evaluated the external precision of such measurements via a recently

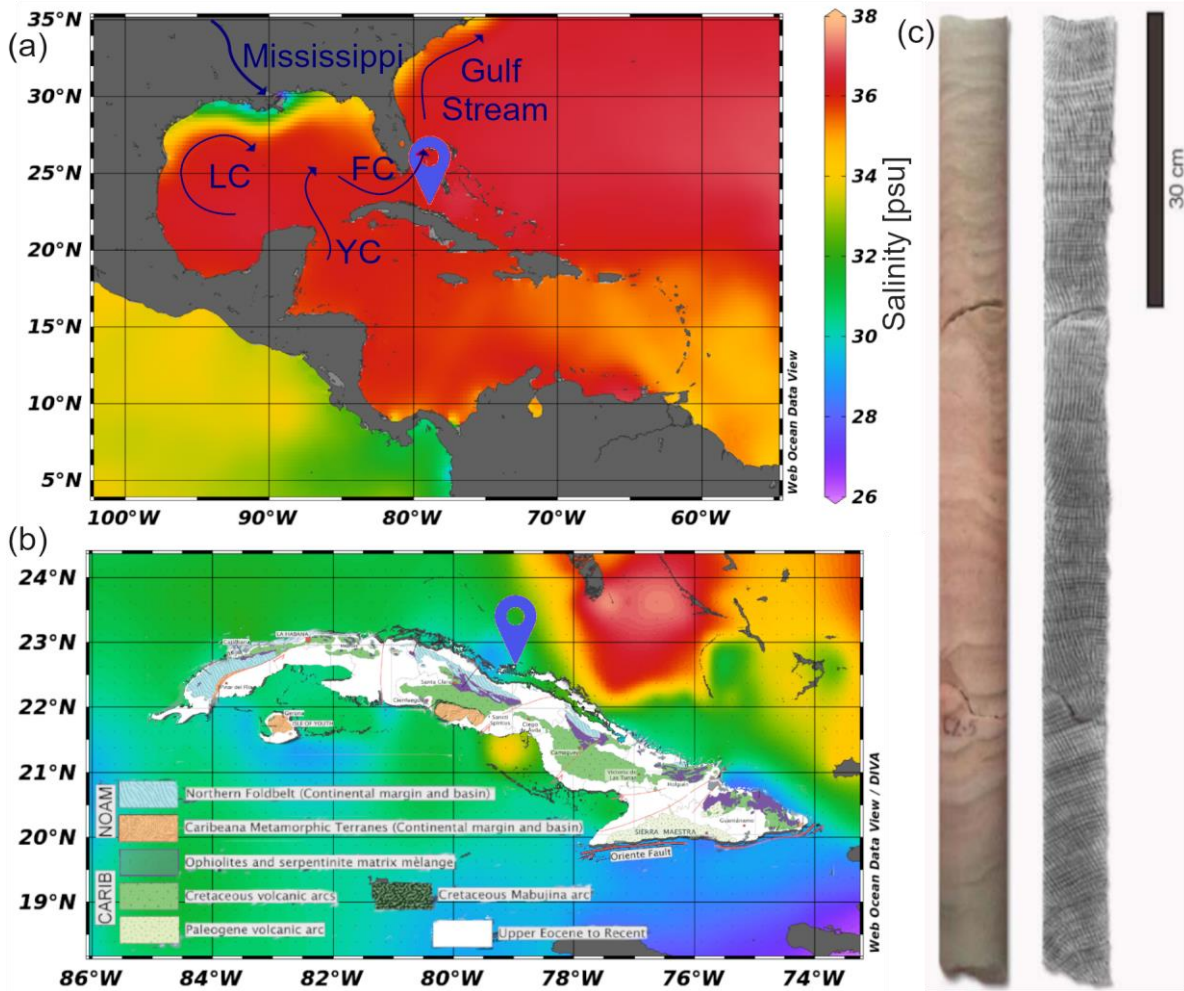
published semi-static data acquisition by Kerber et al. (2023). An external reproducibility of 0.55 ‰ ($2 \sigma_M$) was achieved on seawater and modern aragonitic coral fragments.

To assess the potential impact of shelf water processes on the U isotopic composition of tropical corals and to reveal the potential of U isotopes as freshwater tracer, we selected a long-lived *Orbicella faveolata* coral colony in the western tropical North Atlantic, for which both regional freshwater releases and distant freshwater influence, such as advective transport from the Mississippi River seemed plausible. The tropical Atlantic Ocean is an ideal location for testing potential links between $\delta^{234}\text{U}$ and hydrological and oceanographic conditions at the sub-centennial scale. The northern Caribbean is part of the Atlantic Warm Pool (AWP), which is defined by the sea surface temperature (SST) isotherm exceeding 28.5 °C, which forms each year during early summer (June) and extends into the Gulf of Mexico and the western tropical North Atlantic as summer progresses (July-October) (Wang & Enfield, 2001; Wang et al., 2008). In relation to the AWP and the Intertropical Convergence Zone (ITCZ), the Caribbean hydroclimate is characterized by a wet season from April to October (Martinez et al., 2019), during which hurricanes are also commonly observed (Terry & Kim, 2015). Especially for the Little Ice Age (LIA), which spanned from approximately 1400–1850 (Hodell et al., 2005), substantial changes in the Caribbean SST hydroclimate and potential oceanic circulation have been reconstructed (Haug et al., 2001; Hodell et al., 2005; Richey et al., 2009; Johnson, 2011; Kennett et al., 2012; Fensterer et al., 2013; DeLong et al., 2014; Burn et al., 2016). Consequently, through the study of annual excess ^{234}U variability along a coral core drilled in a colony located at the north of Cuba, we aimed to qualitatively resolve freshwater fluxes into the Gulf of Mexico since the LIA.

2 Material and Methods

85 2.1 Coral location

For this study, we investigated a coral drill core (CSM-1), 97 cm in length, that was collected in March 2016 from the Sabana Camaguey Archipelago, northern Cuba, approximately 20 km from the main island (Fig. 1) (Alonso-Hernández et al., 2022). The core was obtained from a scleractinian coral colony of the genus *Orbicella faveolata* located at approximately 10 m depth in the Cayo Santa María area (79.10 W, 22.66 N). The core was dated via sclerochronology on the basis of radiographic density images, revealing an age of 237 years, ranging from 1778 to 2015 (Alonso-Hernández et al., 2022). The method has an approximate ± 1 yr uncertainty, which may increase progressively with depth from the top of the coral core (Buddemeier et al., 1974). Additionally, the coral exhibited green growth bands with high Mg contents, possibly due to the incorporation of relatively high levels of organic material into the coral skeleton (Cuny-Guirriec et al., 2019; Alonso-Hernández et al., 2022).



95 **Figure 1: (a) Caribbean annual sea surface salinity with the location of the selected coral core on the northern shore of Cuba, directly**
influenced by the Florida Current (FC) travelling eastwards from Yucatan Current (YC) and the Gulf of Mexico forming the Gulf
Stream. The Loop Current (LC) carries the less saline Mississippi water towards the coral. (b) Annual sea surface salinity off the
coast of Cuba; less salinity is observed at the core location due to terrestrial runoff. With generalized geologic-tectonic map of Cuba
modified from (Iturralde-Vinent et al., 2016) (c) X-ray image of the slab used in the optical densitometry analysis and photograph
100 **of the analysed core (CSM-1) with visible green banding.**

The climate of the region is influenced by the southwestern edge of the high-pressure system over the Atlantic (Fig. S1). The summer and fall seasons correspond to the rainy season with occasional extreme events, such as hurricanes. Hurricanes typically track west- and northwards approximately once every 20 years, affecting mainly the southeast coast of Cuba (Limia et al., 2003; Terry & Kim, 2015). During the winter season, the hydroclimate tends to be dry, with precipitation rates decreasing
105 from 250 mm per month in summer to as low as 25 mm per month in winter (Vose et al., 1992).

The location of the sample core lies within the Florida Strait (Fig. 1), serving as the outflow path for water masses from the Gulf of Mexico, with an estimated flow rate of 28 Sv (Leaman et al., 1995). As a result, the coral is influenced primarily by

waters originating from the Caribbean and Gulf of Mexico, as well as very local continental runoff from the northern part of Cuba and eutrophic waters from mangroves bordering the southern key. An additional major yet distant source of freshwater, the Mississippi River, is located approximately 2,500 km away, but its flood plumes can extend hundreds of kilometres into the Atlantic (Hitchcock et al., 1997). This large North American river has an annual discharge rate of 0.015 Sv, which can increase fivefold during major flood events. In addition, the Mississippi carries large volumes of sediment particles, which have halved during the past century due to the creation of dams (Folwell, 1921; Carroll, 1990). The mean $\delta^{234}\text{U}$ value of the Mississippi waters was assessed to be $335 \text{‰} \pm 110 \text{‰}$, including strong seasonal variability (Grzymko et al., 2007).

115 **2.2 Sampling treatment and U extraction**

The separation of uranium from the sample carbonate matrix followed the protocol established by Wefing et al. (2017), with modifications outlined by Kerber et al. (2023). Approximately 50–100 mg of the skeletal aragonite sample underwent ultrasonic cleaning and subsequent dissolution in 7 N HNO_3 . To serve as a concentration reference, 100 μl of TriSpike, a mixture containing the synthetic isotopes ^{233}U , ^{236}U and ^{229}Th , was added. Next, uranium was purified through ion exchange chemistry via U/TEVA resin. To remove Ca and other matrix elements, 300 μl U/TEVA chromatographic ion exchange columns were rinsed three times with 7 N HNO_3 . Uranium was then eluted using 3 N and 1 N HCl successively (Horwitz et al., 1992). The sample was dried and redissolved, and the column purification was repeated until the Ca concentration of the final solution was <10 ppm. For MC-ICP-MS measurements, the final uranium fraction was evaporated and dissolved in 1.2 ml of 1 % HNO_3 + 0.05 % HF, with any particulates removed by centrifugation.

125 **2.3 MC-ICP-MS measurement**

Measurements were conducted at the Institute of Environmental Physics in Heidelberg using a multicollector ICP-MS (ThermoFisher Neptune^{plus}) coupled with an ARIDUS II desolvating nebulizer system and an ESI-SC autosampler. The cup configurations and mounted amplifiers used, as well as the data treatment protocols, are presented in detail in Kerber et al. (2023).

130 Measurements were conducted via the standard bracketing method with the Harwell-Uraninite 1 (HU-1) standard to ensure measurement stability and correct for machine drift. HU-1 was used as an internal bracketing standard for instrumental normalization, its measured $^{234}\text{U}/^{238}\text{U}$ ratio was fixed to a constant reference value during data reduction. This step serves purely as an instrumental correction and does not imply a physical assumption of secular equilibrium. Data evaluation was performed using a Python script for Th/U dating analysis based on Kerber et al. (2025). This script encompasses instrumental background corrections, identification and correction of signal outliers, and adjustment for mass bias, accounting for hydride formation, and addressing tailing and scattering of ^{238}U . $\delta^{234}\text{U}$ was calculated via the processed activity ratio of $^{234}\text{U}/^{238}\text{U}$ and is expressed in per mil (‰) using the following equation (1).

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

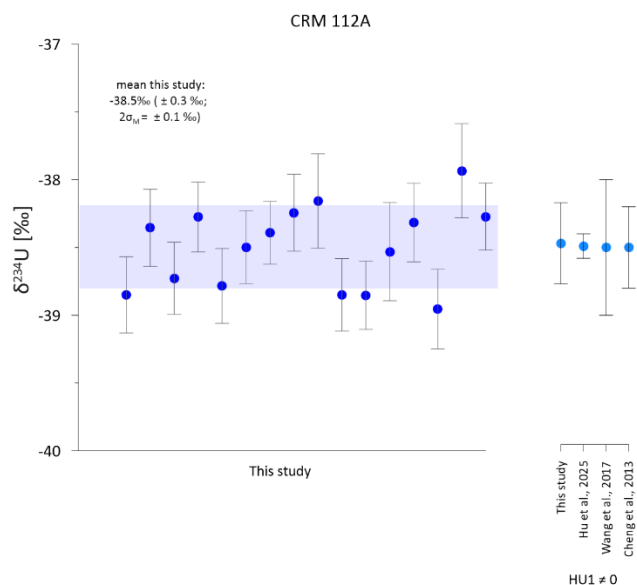
140 with decay constants of $\lambda_{238} = 1.55125 \cdot 10^{-10}$ (Jaffey et al., 1971) and $\lambda_{234} = 2.82206 \cdot 10^{-6}$ (Cheng et al., 2013). This places the data on an activity-based scale defined by the adopted decay constants. Internal errors were determined as 2σ from each measurement, whereas external errors were determined through repeated measurements of the NBS-CRM-112A (CRM112A) standard and an in-house seawater standard.

3 Results

145 3.1 Accuracy

The combined procedural replicates yielded a mean variability of 0.35 ‰, with a 2σ reproducibility of 0.54 ‰ ($n = 6$) in $\delta^{234}\text{U}$ values across replicate groups. The standard deviation from the in-house seawater standard also falls into that range at 0.55 ‰ (2σ , $n = 11$). The external error was determined by repeated measurements of NBS-CRM-112A in each measurement batch. The analyses resulted in a renormalisation of the mean value of $\delta^{234}\text{U}$ (CRM112A) to -38.48‰ ($\pm 0.30 \text{‰}$, $2\sigma_M = \pm 0.17 \text{‰}$, $n = 16$).

150 Figure 2 shows the $\delta^{234}\text{U}$ values of CRM112A. Further advances in coral $\delta^{234}\text{U}$ measurements are described in Greve et al. (in prep.)..



155 **Figure 2: The CRM112A standard was repeatedly measured. The mean value of $-38.5 \text{‰} \pm 0.3 \text{‰}$ is in line with other studies (Cheng et al., 2013; Wang et al., 2017; Hu et al., 2025)**

3.2 Coral samples

Figure 3 shows a total of 104 samples that were collected from the 237-year record of the coral, with each sample representing an integration of one year. These annual samples present a mean $\delta^{234}\text{U}$ value of 145.75 ‰, with a standard deviation of 1.22 ‰. The large data ensemble and small variance contribute to an uncertainty in the mean value of ± 0.24 ‰ ($2\sigma_M$, $n = 104$).
160 This uncertainty of the mean is comparable to that obtained for the CRM112A standard (Fig. 2). The measured mean $\delta^{234}\text{U}$ value of 145.75 ‰ is identical to that of modern seawater (Kipp et al., 2022). Analysis of the small-scale variability within the last 165 years from 1850–2014 reveals a range of 3.32 ‰, from 144.35 ‰ to 147.27 ‰. This variance is 2.5 times greater than that observed in modern seawater (Kipp et al., 2022). Notably, an even higher variability is observed in earlier years, specifically from 1778–1846, during which the $\delta^{234}\text{U}$ values exhibit a total variance of 8.10 ‰, fluctuating from 143.17 ‰ to
165 151.27 ‰.

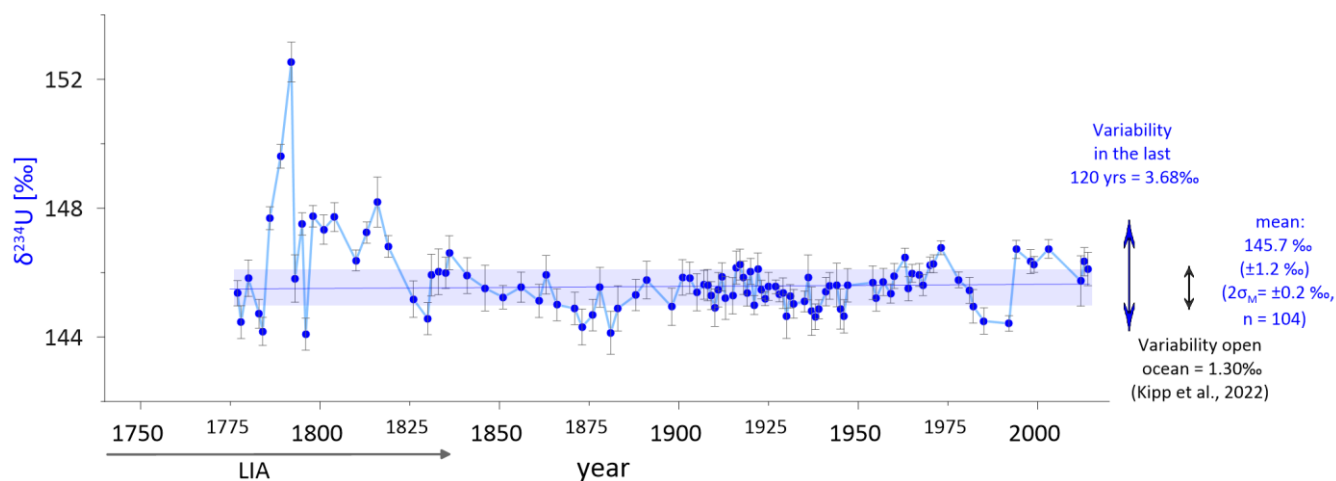


Figure 3: Annual $\delta^{234}\text{U}$ measurements ($n = 104$) of a 237-year-old coral. The mean of 145.75 ‰ (± 0.24 ‰) is identical to the open ocean value of 145.55 ‰ (± 0.28 ‰) (Kipp et al., 2022). The largest deviations from 143.17 ‰ to 151.27 ‰ were observed from 1778–1846 at the end of the Little Ice Age (LIA), with the peak value occurring in 1792. The variability in the coral $\delta^{234}\text{U}$ over the last 165 years is approximately 2.5 times greater than the variance expected from observations in the open ocean (Kipp et al., 2022).
170

4 Discussion

4.1 Seawater $\delta^{234}\text{U}$ from coral aragonite

Corals incorporate the uranium isotopic ratio of seawater ($\delta^{234}\text{U}_{\text{sw}}$) into their skeleton without measurable fractionation (Robinson et al., 2004b; Wang et al., 2017; Kipp et al., 2022). However, one known factor that can cause fractionation is the
175 postdepositional diagenetic alteration of the coral skeletal material (Delanghe et al., 2002; Robinson et al., 2004b; Wang et al., 2017).

Uranium isotope variations in the Cuban coral are independent of growth parameters (e.g., density) or green banding with high Mg concentration (Fig. S3) (Alonso-Hernández et al., 2022). As Mg/Ca is the proxy most sensitive to skeleton diagenesis,

such as calcite or secondary aragonite formation (Allison et al., 2007; Hathorne et al., 2011), the absence of correlation between $\delta^{234}\text{U}$ and Mg/Ca suggests that diagenesis has not influenced the $\delta^{234}\text{U}$ values along the core. Studies have shown that secondary aragonite also has a higher U content than primary skeletal aragonite does (Eggins et al., 2005; Allison et al., 2007; Hathorne et al., 2011), which implies a possible correlation between uranium content and isotopic composition. This correlation was not detected in our results (Table S1 and Fig. S3). Furthermore, a diagenetic overprint could result in extraordinarily high $\delta^{234}\text{U}$ values exceeding 10 ‰ above those of seawater. According to Chutcharavan et al. (2018), a benchmark of 156 ‰ is used to indicate diagenetic alteration of fossil coral material. However, in the coral analysed here, no such elevated values were observed. Consequently, these observations, as well as the excellent agreement of the mean isotopic compositions of corals with those of modern seawater, allow us to conclude that the CSM-1 coral can be used to monitor the U isotopic compositions of local seawater over the past 237 years.

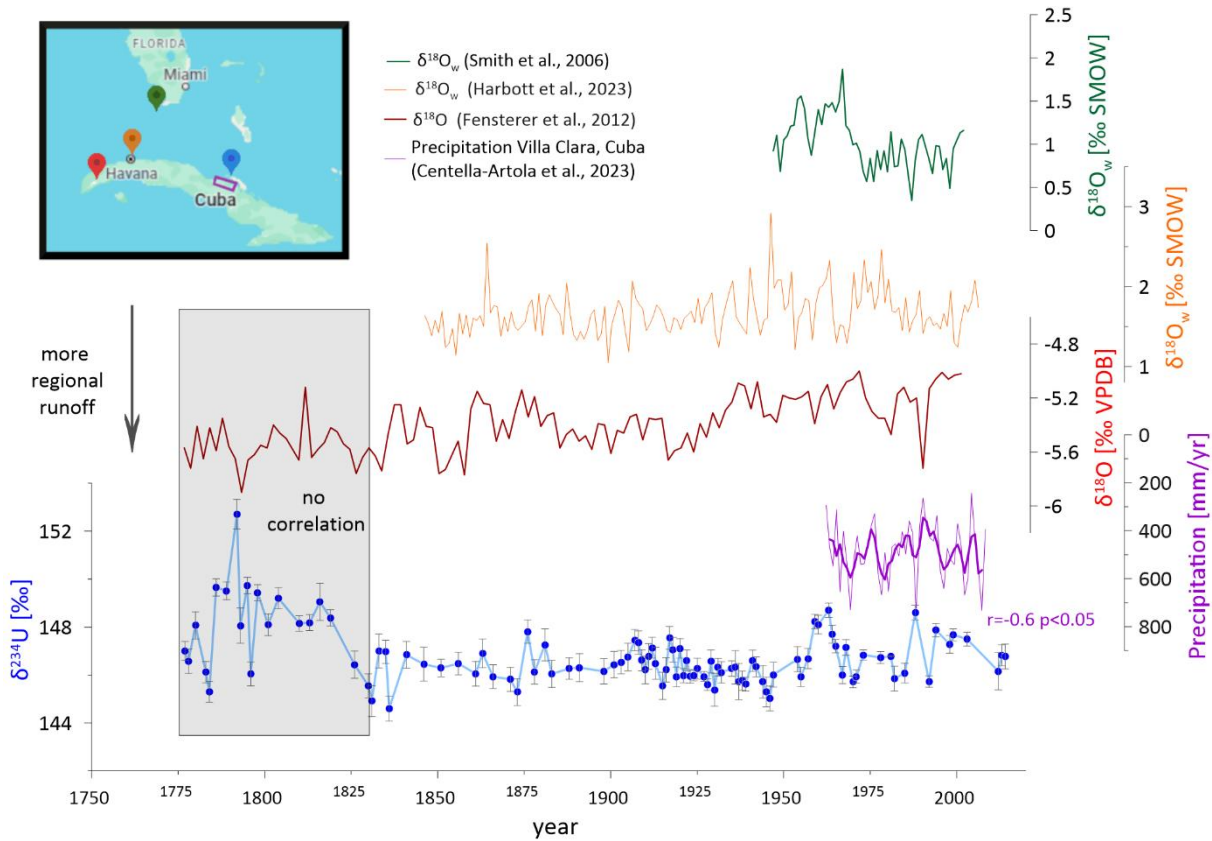
Studies conducted in restricted ocean basins have demonstrated a $\delta^{234}\text{U}$ offset towards higher values, a shift attributed to the substantial influence of meltwater or river discharge (Andersen et al., 2007; Zhou et al., 2015; Wang et al., 2017; Arendt et al., 2018). Despite the Caribbean being a semi-enclosed basin, it receives a high inflow rate of Atlantic waters, estimated at 28 Sv, which exit the Caribbean and Gulf of Mexico near the sample location (Johns et al., 2002). These substantial throughflow rates support the strong control of seawater on the coral mean $\delta^{234}\text{U}$ values.

4.2 Coral $\delta^{234}\text{U}$ values as a proxy for hydrological variation

With excellent reproducibility and overall high precision, even subtle variability can be resolved. The variability in seawater $\delta^{234}\text{U}_{\text{sw}}$ was recently reported to be 1.3 ‰ (Kipp et al., 2022). Under different climate and global weathering conditions, such as during the last sea level low stand and maximum global ice volume, i.e., the Last Glacial Maximum, seawater $\delta^{234}\text{U}_{\text{sw}}$ decreased systematically worldwide by 6 ± 2 ‰ (Henderson, 2002; Esat & Yokoyama, 2006; Chutcharavan et al., 2018). The major sources of isotopic variability in the surface ocean are continental runoff and submerged groundwater. Continental freshwater has a very large range of $\delta^{234}\text{U}$ values from as low as 70 ‰ to 1030 ‰, depending on the continental U cycle driven by erosion and the type of regional weathering (Dunk et al., 2002; Li et al., 2018). In the tropics, chemical weathering prevails, reducing the excess leaching of ^{234}U from the host rock. Moreover, the residence times of freshwater in karstic environments, such as in the Cuban core location, are within days or months to years, resulting in $\delta^{234}\text{U}$ values that are at the lower end of the freshwater scale (Dunk et al., 2002; Paces et al., 2002; Gonzalez-De Zayas et al., 2013; Iturralde-Vinent et al., 2016). Thus, changes in the local freshwater contribution to the ocean could cause the $\delta^{234}\text{U}_{\text{sw}}$ values to shift slightly lower than those of seawater. The annual precipitation from 1960 – 2008 near the coral location has a mean of 482.9 mm yr⁻¹ and varies by approximately 124.5 mm yr⁻¹ (Centella-Artola et al., 2023). Thus, the interannual precipitation variability indicates substantial variations of at least ± 25 % in the local freshwater supply.

Over the past 120 years, the coral record has shown considerable variability on decadal timescales, which is approximately 2–3 times greater than that expected in open ocean seawater (Fig. 3) (Andersen et al., 2010; Kipp et al., 2022). Interestingly, the

$\delta^{234}\text{U}$ variations have exhibited a negative correlation with the regional precipitation record since 1960 ($r = -0.6$ $p < 0.05$, $n = 21$) (Fig. 4) (Centella-Artola et al., 2023).



215 **Figure 4:** The $\delta^{234}\text{U}$ values from the analysed coral in central northern Cuba (blue) are negatively correlated ($r = -0.60$, $p < 0.05$) with
 220 a precipitation record from the same region, starting in 1960 (purple; inverted y-axis) (Centella-Artola et al., 2023). Similar patterns
 are observed with $\delta^{18}\text{O}_w$ values calculated from corals from southern Florida (green) (Smith et al., 2006) and northern Cuba (orange)
 (Harbott et al., 2023), with high $\delta^{234}\text{U}$ values corresponding to high $\delta^{18}\text{O}_w$ values. Additionally, since 1860, there has been a similar
 trend in the $\delta^{18}\text{O}$ values from a stalagmite in northwestern Cuba, which are interpreted as a precipitation indicator (red) (Fensterer
 et al., 2012). These alignments show a visible influence of precipitation on the $\delta^{234}\text{U}$ values of the coastal waters in which the coral
 lived, with low $\delta^{234}\text{U}$ values representing greater runoff influences. In the period from 1778–1860, there appears to be no such trend
 between the stalagmite record and the coral record, likely indicating a substantial marine influence on the coral during the end of
 the Little Ice Age.

225 These subtle variations in $\delta^{234}\text{U}$ are close to the reproducibility limit of the U isotope measurements but are still statistically
 noteworthy. The local $\delta^{234}\text{U}_{\text{SW}}$ value is dependent on the input of terrestrial sourced freshwater, such as river runoff and
 submarine groundwater discharge. In Cuba, the residence time of precipitated water is relatively short and in the range of days
 to months due to the karstic terrain (Gonzalez-De Zayas et al., 2013; Iturralde-Vinent et al., 2016). Uranium isotopic
 compositions in groundwater are influenced by both redox conditions and uranium concentrations. Typically, an inverse
 relationship exists between groundwater uranium concentration and $\delta^{234}\text{U}$; deep, reducing groundwaters with low uranium
 concentrations tend to show higher $\delta^{234}\text{U}$ values than oxic, near-surface waters with higher concentrations (Osmond & Cowart,

230 1976; Asikainen, 1981). Redox conditions also influence uranium mobility and isotope fractionation, with well-oxidizing groundwaters yielding lower activity ratios (Suksi et al., 2006). Catchment-scale denudation further affects these ratios: a U-shaped relationship has been observed, where both low and high denudation rates correspond to elevated $\delta^{234}\text{U}$ values, while intermediate rates yield lower values (Li et al., 2018). Studies from the Yucatán Peninsula and Tampa Bay, Florida, have reported low $\delta^{234}\text{U}$ values in groundwater and estuarine waters, which also showed relatively high uranium concentrations

235 (Osmond & Cowart, 2000; Swarzenski & Baskaran, 2007; Schorndorf et al., 2023). The low $\delta^{234}\text{U}$ values in the coral may therefore reflect shallow groundwater runoff influenced by oxidizing conditions and/or moderate denudation rates in riverine waters in the region. Hence, the freshwater runoff coming from the Carbonate Hinterland (Iturralde-Vinent et al., 2016) and related to precipitation may lead to a moderate decrease of $\delta^{234}\text{U}$ values in coastal seawater. This process likely explains the anticorrelation of coral $\delta^{234}\text{U}$ values, where lower $\delta^{234}\text{U}$ values coincided with high annual precipitation over the last 50 years

240 (Fig. 4). A study of a sediment core situated approximately 100 km east of the analysed coral core revealed a freshwater influence on organic matter by approximately 15 % from 1900–1970 (Alonso-Hernández et al., 2022). During this time, the coral exhibited a mean $\delta^{234}\text{U}$ of 145.25 ‰, at the lower limit of open ocean seawater, possibly reflecting a persistent but minor local freshwater influence. The influence on $\delta^{234}\text{U}$ is likely far lower than that observed for organic matter by Alonso-Hernández et al. (2020) because of the lack of high-discharge rivers nearby.

245 A commonly used proxy for sea surface salinity is stable oxygen isotopes in seawater ($\delta^{18}\text{O}_{\text{sw}}$), as they depend on both freshwater influx and evaporation (Leder et al., 1996; Gagan et al., 1998; Gagan et al., 2000; Ren et al., 2003). A comparison with reconstructed $\delta^{18}\text{O}_{\text{sw}}$ values from tropical corals in proximity to the sample location also revealed similarities at annual time scales (Fig. 4) (Table S2) (Smith et al., 2006; Harbott et al., 2023). The $\delta^{18}\text{O}_{\text{sw}}$ is calculated from the measured coral $\delta^{18}\text{O}$ values (Smith et al., 2006), which are influenced by seawater $\delta^{18}\text{O}_{\text{sw}}$ and temperature. By subtracting the temperature component derived from the Sr/Ca record of the same coral, the $\delta^{18}\text{O}_{\text{sw}}$ at the time of coral growth can be calculated (Ren et al., 2003). Note that the SST, estimated via the Li/Ca ratio (Alonso-Hernández et al., 2022), is not significantly correlated with the coral $\delta^{234}\text{U}$ values (Fig. S2).

250 For the 19th century, the coral $\delta^{234}\text{U}$ values aligned with the $\delta^{18}\text{O}$ record of a stalagmite from western Cuba, interpreted as a proxy for rainfall amount (Fensterer et al., 2012). This alignment falls within the uncertainty of the stalagmite age model (Fig.

255 4). Before 1860, the stalagmite and coral records diverged from one another, suggesting a potential additional source of $\delta^{234}\text{U}$ and its variability. Here, we propose that this source is linked to distant freshwater discharge from the North American continent and/or a synchronous reduction in the strength of the Gulf of Mexico current, which is not traced by the hydroclimate record of the stalagmite.

4.3 Variability during the LIA

260 The highest variability in the coral $\delta^{234}\text{U}$ values occurred between 1778 and 1846, with $\delta^{234}\text{U}$ values ranging from 144.1 ‰ to 152.5 ‰. This time interval of high $\delta^{234}\text{U}$ variability coincides with the end of a period of colder SSTs in the Caribbean during the LIA (Winter et al., 2000; Haase-Schramm et al., 2003; Kilbourne et al., 2008).

4.3.1 Fast and high local runoff

Some studies inferred reduced precipitation during the LIA, including Haug et al. (2001) for the southern Caribbean, Hodel et al. (2005) for the Yucatan Peninsula and Richey et al. (2009) for the Gulf of Mexico. However, other studies have reported highly variable amounts of rainfall in the northern part of the Caribbean and the Gulf of Mexico (Kennett et al., 2012; Fensterer et al., 2013; DeLong et al., 2014; Burn et al., 2016). Historical records in Cuba also documented periods of drought interspersed with several severe hurricanes in the late 1700s (Johnson, 2011) (Fig. 5). A high amount of local precipitation with fast discharge rates can explain the low $\delta^{234}\text{U}$ values recorded in the coral, as discussed above. The punctuated low values recorded by the coral suggest multiple local extreme precipitation events, particularly from 1778–1847 (Fig. 5). Wang and Enfield (2001) reported that an extended Atlantic Warm Pool fuels precipitation and the frequency of more intense tropical storms. Additionally, DeLong et al. (2014) linked fluctuating SSTs in Dry Tortugas and Puerto Rico (Kilbourne et al., 2008) to a variability in the size of the western hemispheric warm pool. The reconstructed SST from the Li/Ca in the analysed coral also exhibited high variability during that time (Alonso-Hernández et al., 2022). Therefore, fluctuating $\delta^{234}\text{U}$ values further support times of fast and high local runoff.

Another possible influence on the $\delta^{234}\text{U}$ values is land use change on the Cuban island. Beginning around 1820, widespread deforestation was undertaken to expand sugarcane cultivation (Monzote, 2008). This deforestation likely increased soil erosion and enhanced continuous runoff into coastal waters (Monzote, 2024). Prior to widespread deforestation, uranium delivery to coastal waters was limited in magnitude and more episodic, as forest cover suppressed soil erosion and regulated hydrological fluxes (Palmer & Edmond, 1993; Zhang et al., 2023). Under these conditions, the isotopic composition of uranium was strongly influenced by local lithological heterogeneity. Inputs derived from shallowly weathered soils would have carried elevated $\delta^{234}\text{U}$ values due to preferential leaching of ^{234}U , whereas contributions from less-weathered bedrock or carbonate units closer to secular equilibrium could have lowered ^{234}U toward or below the marine mean (Chabaux et al., 2008; Li et al., 2018). The archive therefore records large variability, including excursions to relatively low $\delta^{234}\text{U}$ values, reflecting the sensitivity of the system to short-term and spatially heterogeneous sources.

Following the onset of large-scale deforestation in the early nineteenth century, enhanced and continuous soil erosion generated a greater and more sustained flux of weathering-derived uranium to the coastal environment (Chabaux et al., 2008; Li et al., 2018; Monzote, 2024). Because ^{234}U is preferentially mobilized during chemical weathering, this terrestrial input typically carried $\delta^{234}\text{U}$ values above equilibrium (Chabaux et al., 2008; Li et al., 2018). The larger and more consistent flux buffered the

290 influence of localized or episodic inputs, leading to a stabilization of $\delta^{234}\text{U}$ values in the archive and their convergence toward
the oceanic mean.

Figure 5 shows the Ba/Ca record of the coral core, exhibits a positive covariation with the $\delta^{234}\text{U}$ record except for a particular
strong Ba/Ca peak surrounding the year 1820 to 1830. The correspondence suggests that both proxies respond to a common
environmental driver, potentially linked to changes in terrigenous input or nearshore hydrographic conditions. Periods of
295 enhanced Ba/Ca and $\delta^{234}\text{U}$ broadly coincide with phases of precipitation extremes until 1820, when Ba/Ca decouples from
 $\delta^{234}\text{U}$. This event coincides with intensified land-use change on Cuba, including widespread deforestation after 1820, which has
been shown to increase soil erosion and the export of particulate and dissolved material to the coastal ocean. During the same
time interval, precipitation moderately increases as indicated by the speleothem $\delta^{18}\text{O}$ values (Fig. 4). Obviously Ba/Ca response
more sensitive to such local vegetation and soil changes that coincide with precipitation changes as compared to $\delta^{234}\text{U}$, which
300 does not reveal a significant increase during those years.

Therefore, the lack of synchronous variability between the coral $\delta^{234}\text{U}$ record and the stalagmite $\delta^{18}\text{O}$ record from Cuba
(Fensterer et al., 2012) suggests that local precipitation changes can unlikely explain the observed $\delta^{234}\text{U}$ variability between
the years 1780 - 1850. Together, these observations imply that the $\delta^{234}\text{U}$ signal recorded in the coral reflects marine and to a
lesser degree regional land-use-related influences rather than a simple response to island-scale rainfall variability.

305

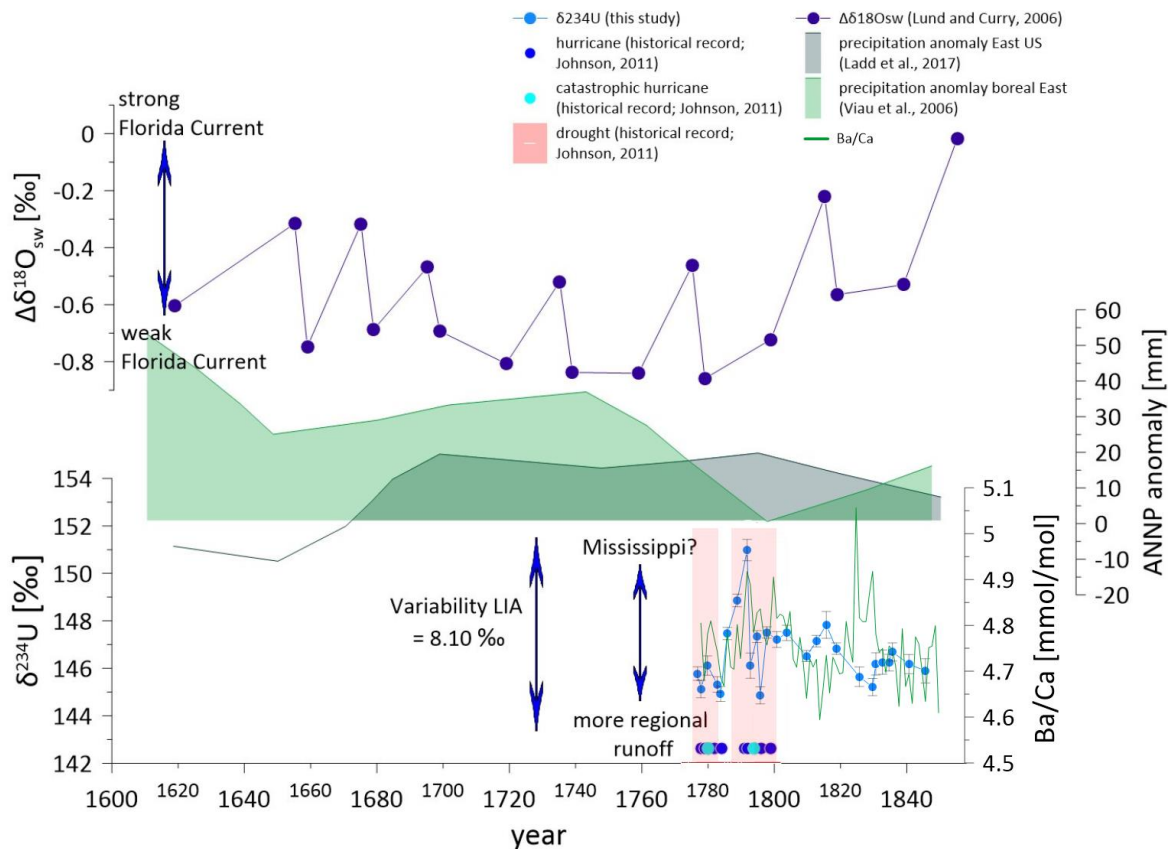


Figure 5: $\delta^{234}\text{U}$ values (blue) from 1778–1850 plotted together with the timing of hydrological events documented in historical records (Johnson, 2011), indicating times of high hydrological fluctuation with droughts (red), hurricanes (dark blue), and catastrophic hurricanes (light blue). The green line shows Ba/Ca ratios of the coral core corresponding to the $\delta^{234}\text{U}$ values. Florida Current strength is inferred from $\Delta\delta^{18}\text{O}_{\text{sw}}$ differences between the Gulf of Mexico and the Bahamas Channel (purple; (Lund & Curry, 2006)), where more negative values reflect a weaker current during the LIA. Superimposed precipitation anomalies over eastern North America (dark green; (Ladd et al., 2018)) and the boreal east (light green; (Viau et al., 2006)) show enhanced precipitation during this same interval, consistent with a weakened Florida Current and elevated variability in $\delta^{234}\text{U}$ values.

315 4.3.2 Possible Mississippi influence

With a smaller warm pool, precipitation over the eastern North American continent has increased due to changes in atmospheric circulation (Wang et al., 2008; Ladd et al., 2018). This enhancement also extended to parts of the Mississippi recharge basin (Ladd et al., 2018), potentially leading to increased runoff. The Mississippi River was found to have elevated $\delta^{234}\text{U}$ values averaging approximately 335 ‰, with strong seasonal variations and values reaching up to 450 ‰ (Grzymko et al., 2007).

320 During the end of the LIA, the coral $\delta^{234}\text{U}$ values are frequently elevated by > 3 ‰ compared with those in the mean ocean and are even more significant than those in locally depleted runoff. Thus, we hypothesize that these elevated $\delta^{234}\text{U}$ values resulted from ^{234}U -enriched waters from Mississippi that reached the Gulf of Mexico and induced excess ^{234}U to the coral site. Upon discharge, the river plume is carried westward and southwestward along the Louisiana-Texas shelf within the Gulf's

325 general cyclonic circulation, often described as the Mexican Current system, which flows counter to the eastward Loop Current
(Androulidakis & Kourafalou, 2013). Although this circulation pattern tends to retain Mississippi-derived material within the
western Gulf, episodic entrainment into the Loop Current has been documented during periods of strong eddy activity or
northward Loop Current extensions (Muller-Karger, 2000; Morey et al., 2003; Androulidakis & Kourafalou, 2013). Once
incorporated into the Loop Current, dissolved constituents such as uranium could be transported eastward through the Florida
Strait and subsequently redistributed in the southern Florida Strait along the northern Cuban shelf (Fratantoni et al., 1998;
330 Androulidakis et al., 2020). Indeed, analysis of satellite salinity measurements indicates, that Mississippi-sourced waters can
extend as far as the Florida Straight (Cummings & Smedstad, 2013). Because uranium in seawater is conservative, with a
residence time on the order of 400–500 kyr (Jaffey et al., 1971; Chen et al., 1986), inputs from the Mississippi would rapidly
mix with the surrounding marine reservoir. While this makes it unlikely that Mississippi-derived uranium dominated the local
isotopic budget, periodic variability of the Loop Current or increased fluvial fluxes could have enhanced its relative
335 contribution. Such variability may have contributed to shifts in $\delta^{234}\text{U}$ values at the site, particularly prior to the stabilization
associated with nineteenth-century land-use change on Cuba and under differing oceanographic settings.

The LIA likely made the Gulf of Mexico-Caribbean system more dynamic and variable. Periods of stronger winds and
increased Mississippi River discharge would have enhanced the eastward advection of river water across the northern Gulf
and its subsequent entrainment into the Loop Current, favouring export toward the Straits of Florida and the northern Cuban
340 shelf (Muller-Karger, 2000; Morey et al., 2003). At the same time, wind forcing and Caribbean eddies exert strong control
over Loop Current extension and eddy shedding, at times shortening the shedding period to 3–7 months or prolonging it to
14–16 months (Oey et al., 2003). Thus, while enhanced storminess and runoff during the LIA may have increased the potential
for Mississippi River influence on Cuban shelf waters, alternating phases of Loop Current suppression by Caribbean
anticyclones would have periodically dampened this transport. Explaining the high variability in the $\delta^{234}\text{U}$ values from the
345 coral during the End of the LIA.

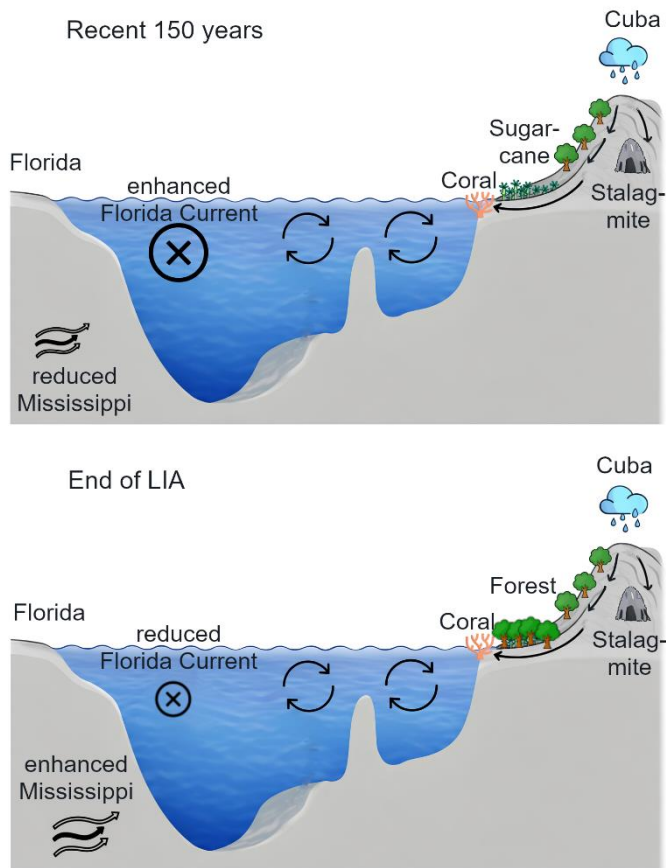
A strong Caribbean current would more efficiently dilute any freshwater signal than a reduced Gulf of Mexico throughflow.
During the LIA, Lund et al. (2006) reported a decrease in the throughflow rate at the Florida Strait by approximately 10 %,
predominantly in the wind-driven part of the Florida Current. This reduction, coupled with an increase in precipitation over
the eastern part of the North American continent (Lund et al., 2006; Ladd et al., 2018), could reasonably account for a higher
350 total U discharge from the Mississippi River. This scenario likely contributed to the observed punctuated increase in $\delta^{234}\text{U}$
values of 2–3 ‰ during the LIA. Lund and Curry (2006) and Richey et al. (2009) further suggested saltier conditions in the
Gulf of Mexico during the LIA, bringing the Caribbean Basin closer to today's conditions of semi-enclosed basins such as the
Mediterranean Sea. These basins present elevated $\delta^{234}\text{U}$ values due to restricted access from open ocean seawater, high
evaporation rates and the input of much freshwater and submerged groundwater from terrestrial sources (Border, 2020).
355 However, changes in throughflow of up to 10 % are small overall compared with possible major changes in U runoff and its
isotopic composition.

Given the capacity for Ba and other trace elements to be transported over large distances within the Gulf of Mexico, enhanced influence of the Mississippi River plume represents a plausible cause for the correlation of Ba/Ca and $\delta^{234}\text{U}$ in the coral core observed at the end of LIA, with the exception of a local induced strong Ba/Ca increase from deforestation over the years 1820 to 1830.

This interpretation is consistent with the absence of coherent variability between the coral $\delta^{234}\text{U}$ record and the Cuban stalagmite $\delta^{18}\text{O}$ record (Fensterer et al., 2012), which argues against island-scale precipitation and local runoff as the dominant controls. Instead, the decoupling of these records points toward a stronger role for large-scale river discharge and marine transport processes of U into the Gulf of Mexico as a whole. In this context, increased Mississippi uranium runoff into the Gulf of Mexico during the terminal phase of the LIA, potentially associated with enhanced meltwater and sediment fluxes from higher latitudes, provides a viable explanation for the elevated $\delta^{234}\text{U}$ values observed during this interval.

The discussion above assumes that the $\delta^{234}\text{U}$ values in the coral are influenced solely by Mississippi freshwater and seawater, neglecting the potential impact of other sources with different $\delta^{234}\text{U}$ ratios. The reduced wind-driven portion of the Florida Current, which originates from the North Atlantic Subtropical Gyre (Lund et al., 2006), results in a greater contribution of South Atlantic sourced water, potentially affecting the coral $\delta^{234}\text{U}$ ratios. South Atlantic waters are further influenced by the significant discharge of the Amazon and Orinoco rivers near the entrance of the Caribbean (Vorosmarty et al., 1998; Paterne et al., 2023). The Amazon River has elevated $\delta^{234}\text{U}$ values of 204 ‰ (± 4 ‰) (Swarzenski et al., 2004; Border, 2020). However, a study of uranium concentrations and $\delta^{234}\text{U}$ values in the Amazon delta identified an uranium sink due to anaerobic conditions (Border, 2020), suggesting that Amazon-derived uranium does not have a significant large-scale influence on Cuban corals. Changes in Florida Current strength may have influenced the residence time of river-derived signals within the Gulf of Mexico. However, circulation changes alone are unlikely to generate the observed elevation in $\delta^{234}\text{U}$ values without the presence of a high- $\delta^{234}\text{U}$ freshwater endmember. The Mississippi River represents such a source of isotopically enriched uranium injected into the Gulf of Mexico and its variability is consistent with the observed covariance between Ba/Ca and $\delta^{234}\text{U}$ in the coral record. Taken together, the available constraints are most consistent with enhanced Mississippi discharge as a principal contributor to the late LIA $\delta^{234}\text{U}$ variability, with circulation changes influencing the magnitude and expression of the signal. These changes end around the year 1820, when global temperatures start increasing. Between 1820 to 1830 rapid local deforestation of the Cuba Island caused a pulse of Ba runoff to the ocean.

Further spatially resolved $\delta^{234}\text{U}$ records, particularly from sites proximal to the Mississippi River mouth such as Flower Garden Banks (DeLong et al., 2023), would allow quantitative evaluation of the predicted fluvial gradient and help constrain the relative contributions of discharge versus circulation changes. Additional groundwater characterization and broader Caribbean coral records would refine the regional hydrographic context of the late LIA variability.



390 **Figure 6: Schematic comparison of environmental conditions during the end of the Little Ice Age (LIA) and the last ~150 years. The lower panel depicts the terminal LIA, characterized by enhanced Mississippi River discharge, reduced Florida Current strength, and predominantly forested land cover in Cuba. The upper panel represents the recent period, with reduced Mississippi influence, strengthened Florida Current transport, and expanded agricultural land use in Cuba. Arrows indicate relative changes in river input, ocean circulation, and terrestrial runoff pathways affecting the coral site north of Cuba.**

5 Conclusion

395 This study presents the first annually resolved coral $\delta^{234}\text{U}$ record spanning 237 years of seawater $\delta^{234}\text{U}$ from the northern part of Cuba, which was obtained via analysis of the uranium isotopic composition along a coral core of *Orbicella faveolata*. Our results confirm that coral $\delta^{234}\text{U}$ reliably records the seawater composition ($\delta^{234}\text{U}_{\text{SW}}$) without significant diagenetic alteration, as evidenced by the lack of correlation between $\delta^{234}\text{U}$, density and Mg/Ca ratios. The coral has a mean $\delta^{234}\text{U}$ value of 145.74 ‰ (± 0.2 ‰), which is identical to the open ocean value of 145.55 ‰ (± 0.28 ‰). Decadal $\delta^{234}\text{U}$ variations are approximately 2–3 times greater than those in open ocean seawater and correlate inversely with regional precipitation since 1960 ($r = -0.6$, p

400 < 0.05), suggesting an influence of local terrestrial freshwater input, likely from surface runoff and submerged groundwaters. From 1778–1846, coinciding with the end of the Little Ice Age, the $\delta^{234}\text{U}$ record exhibited high variability, with values ranging from 143.40 ‰ to 151.50 ‰, which suggests substantial hydrological changes characterized by severe droughts and increased hurricane activity. Changes in atmospheric circulation during that time also led to increased precipitation over the eastern North American continent, including the Mississippi drainage basin. Thus, elevated $\delta^{234}\text{U}$ values are potentially related to
405 stronger winds and increased freshwater input from the Mississippi River, and reduced throughflow in the Florida Strait, which have enhanced the potential for river water to reach the northern Cuban shelf. And caused a 2–3 ‰ increase in coral $\delta^{234}\text{U}$, which a greater variability during the end of the LIA. However, the influence of other far more distant freshwater sources, such as the Amazon River, was likely minimal due to localized uranium sinks. This study highlights the potential of coral $\delta^{234}\text{U}$ as a promising proxy for reconstructing past hydrographic and riverine variability.

410

Credit authorship contribution statement

SG: conceptualization, data production, interpretation and writing

NF: conceptualization, MC-ICPMS support, mentoring, and data quality control

SW: conceptualization, and hydroclimate records from speleothems

415 PM: sample supply, SST calculation and trace element measurement

ED: trace element measurement

CAH: sample supply, SST calculation

MGB: sample supply

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Open research

The raw data of the figures and tables presented in this paper are found in the Supplement and at the PANGAEA open data
425 library (<https://doi.pangaea.de/10.1594/PANGAEA.973159>).

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