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

Reviewer 1 comment:

The paper by Greve et al presents a very neat record of $\partial^{234}U$ variability within a coral core from northern Cuba, whose variability is interpreted to reflect hydrological changes. The manuscript includes an analytical validation of the methodology, to verify that the observed variability of few permil is beyond the analytical uncertainty and are accurate. The authors also compare the results to a contemporaneous $\partial^{18}O$ record from a stalagmite collected from a nearby cuban cave.

I find the work very interesting and worth publishing, yet I find that most of the hypothesis about the potential processes controlling $\partial^{234}U$ in the coral somewhat speculative and more evidence about the processes that might be controlling $\partial^{234}U$ in seawater would be required to make a stronger case.

Response:

We thank the reviewer for the encouraging comments.

We fully agree that additional evidence on the controlling mechanisms of $\delta^{234}U$ in seawater would substantially strengthen the interpretation. The primary aim of this study, however, is to robustly document and validate the presence of small but significant $\delta^{234}U$ variability in a well-dated coral archive and to demonstrate that this variability exceeds analytical uncertainty and results from local to regional modulations of the seawater $\delta^{234}U$ composition. Given the general complexity of the hydrographic and geochemical setting in coral reefs and here in the northern Caribbean, we therefore intentionally limit our conclusions regarding specific controlling mechanisms and instead discuss a range of plausible drivers without favouring a single process. We acknowledge that the use of Ba/Ca for the period of the LIA has broad in further support to local versus distant influences on the $\delta^{234}U$ ratio recorded by the coral.

We will clarify these aspects in the revised manuscript to emphasize that our discussion is exploratory rather than conclusive by adding:

"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 $\delta^{234}U$ 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 $\delta^{234}U$ record and the Cuban stalagmite $\delta^{18}O$ 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 $\delta^{234}U$ values observed during this interval."

“Changes in Florida Current strength may have influenced the transport efficiency and residence time of river-derived signals within the Gulf of Mexico. However, circulation changes alone are unlikely to generate the observed elevation in $\delta^{234}U$ values without the presence of a high-$\delta^{234}U$ freshwater endmember. The Mississippi River represents such an enriched source and its variability is consistent with the observed covariance between Ba/Ca and $\delta^{234}U$ in the coral record. Taken together, the available constraints are most consistent with enhanced Mississippi discharge as a principal contributor to the late LIA $\delta^{234}U$ variability, with circulation changes influencing the magnitude and expression of the signal.

Further spatially resolved $\delta^{234}U$ 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.”

We also note that a dedicated follow-up project, recently funded by the German Research Foundation (DFG), will specifically address the processes controlling $\delta^{234}U$ variability in this region and represents the logical next step to reduce the remaining speculative aspects.

Reviewer 1 comment:

It would be interesting, for example, to compare to other geochemical proxies in the coral itself, like REE or other trace elements to verify or rule out other processes.

Response:

We agree that additional geochemical tracers are valuable. In response to this suggestion, we have added first Ba/Ca data covering the interval of most pronounced $\delta^{234}U$ variability. While Ba/Ca shows a positive relationship with $\delta^{234}U$, this relationship does not allow us to uniquely identify a specific controlling mechanism, but it allows to exclude local deforestation as the major source to $\delta^{234}U$ changes. This is primarily because Ba can be supplied not only by local terrestrial runoff but also by distal sources such as the Mississippi River plume, but its sensitivity to local processes is much higher. We will expand the discussion accordingly to explicitly address these limitations:

“Figure 5 shows the Ba/Ca record of the coral core, exhibits a positive covariation with the $\delta^{234}U$ 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 enhanced Ba/Ca and $\delta^{234}U$ broadly coincide with phases of precipitation extrems until 1820, when Ba/Ca decouples from $\delta^{234}U$. This event coincids 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 $\delta^{18}O$ values (Fig. 4). Obviously Ba/Ca response more sensitive to such local vegetation and soil changes that coincide with precipitation changes as compared to $\delta^{234}U$, which does not reveal a significant increase during those years.

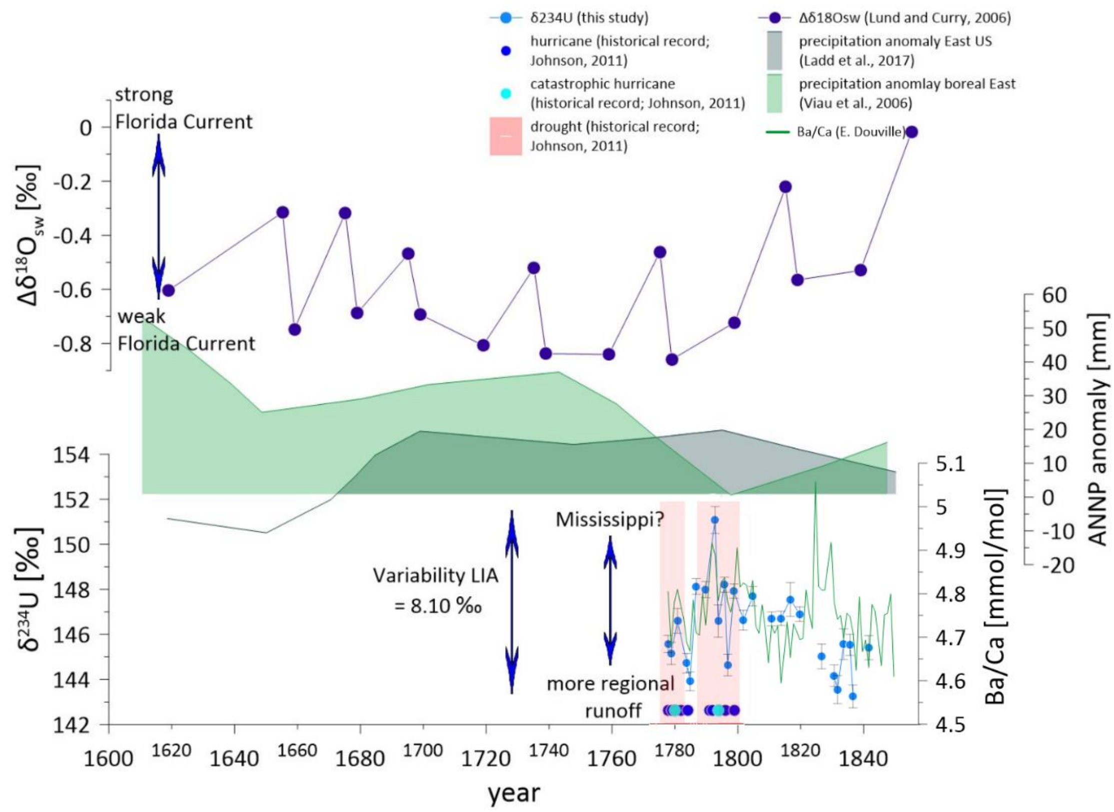

Figure 5: $\delta^{234}U$ values (blue) from 1778–1830 plotted together with the timing of hydrological events documented in historical records (Johnson, 2011), indicating times of high hydrological fluctuation with droughts (red), hurricanes (dark blue), and catastrophic hurricanes (light blue). The green line shows Ba/Ca ratios of the coral core corresponding to the $\delta^{234}U$ values. During these times, the $\delta^{234}U$ values exhibited high variability, ranging from 143.40 ‰ to 151.50 ‰ in 1792. According to the present age model this high value occurred during a period of recurrent major hurricanes. Florida Current strength is inferred from $\Delta\delta^{18}O_{sw}$ 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 $\delta^{234}U$ values."

Reviewer 1 comment:

Whilst the comparisons with the d18O record from the stalagmite and the other rainfall records are interesting, I find it not very compelling and stronger evidence would enhance the author's conclusions. The fact that the period with highest $\partial^{234}U$ is not correlated with the rainfall record deserves further exploration

Response:

We appreciate this critical assessment and the request for further exploration. A single stalagmite $\delta^{18}O$ record cannot provide a one-to-one correspondence with the Cuban precipitation and discharge and therefore neither with the coral $\delta^{234}U$ signal. We attempted to interpret this comparison cautiously and primarily use it to illustrate the regional hydroclimatic context rather than as direct mechanistic evidence. The lack of correlation during the interval of highest $\delta^{234}U$ will be more explicitly discussed, and we emphasize that this decoupling likely reflects the increasing dominance of marine versus local terrestrial signals at the coral site also seen in the Ba/Ca ratio of this coral.

We also acknowledge the reviewer's important point that the cave record represents a different hydrographic setting with likely limited influence from historical deforestation.

Accordingly, we clarify in the revised manuscript that the stalagmite record cannot be used to tightly constrain the δ^{234}U controlling mechanisms at the reef site.

"Therefore, the lack of synchronous variability between the coral δ^{234}U record and the stalagmite δ^{18}O record from Cuba (Fensterer et al., 2012) suggests that local precipitation changes can unlikely explain the observed δ^{234}U variability between the years 1780 - 1850. Together, these observations imply that the δ^{234}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.

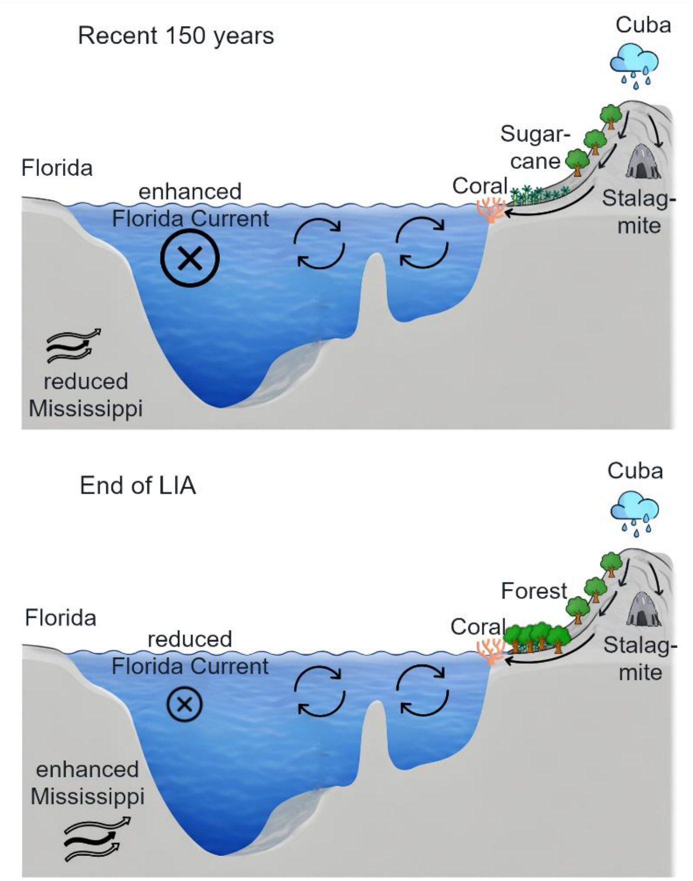

Figure 6: Schematic comparison of environmental conditions during the end of the Little Ice Age (LIA) and the last ~150 years. The lower panel depicts the terminal LIA, characterized by enhanced Mississippi River discharge, reduced Florida Current strength, and predominantly forested land cover in Cuba. 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."

Reviewer 1 comment:

The authors make a strong case to explain who the elevated ∂^{234}U from the Mississippi river are being diluted and only during times of significant runoff increments the high ∂^{234}U values might reach the reef area. However, it would be interesting to determine if this is because increased sediment load into the reef, dissolved sediment (or both, I assume that Th was also measured in some samples?). I would also hypothesize that the increased ∂^{234}U at the end of the Little Ice Age might be the result from increased runoff from the Mississippi from melting ice and snow at higher latitudes in continental North America, whilst the increased ∂^{234}U at the end of the end of the XX century might be the result form increasingly larger sediment loads from increased oil extraction in the Gulf of

Mexico (which could be tested with Ba analyses in the core as $BaSO_4$ is usually used as lubricant during oil drilling.

Response:

We appreciate these stimulating hypotheses. As noted above, we have included Ba/Ca data for the period of pronounced $\delta^{234}U$ variability. Although Ba/Ca covaries positively with $\delta^{234}U$ from 1780 to 1820, it does not allow us to unambiguously differentiate between increased runoff, sediment remobilization, or anthropogenic inputs, given the multiple potential Ba sources in the region. In addition, oil extraction from shallow shelf environments only started in 1938 and took a larger share in the mid-80s oil crisis. Thus, for the period of the past 250 years this evolution could be visible in the Ba/Ca as suggested, for which we presently lack information. Moreover, this would make any interpretation of runoff proxies even more complex. We therefore refrain from further interpretation along these lines in the current manuscript.

"Figure 5 shows the Ba/Ca record of the coral core, exhibits a positive covariation with the $\delta^{234}U$ 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 enhanced Ba/Ca and $\delta^{234}U$ broadly coincide with phases of precipitation extrems until 1820, when Ba/Ca decouples from $\delta^{234}U$. This event coincids 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 $\delta^{18}O$ values (Fig. 4). Obviously Ba/Ca response more sensitive to such local vegetation and soil changes that coincide with precipitation changes as compared to $\delta^{234}U$, which does not reveal a significant increase during those years.

Therefore, the lack of synchronous variability between the coral $\delta^{234}U$ record and the stalagmite $\delta^{18}O$ record from Cuba (Fensterer et al., 2012) suggests that local precipitation changes can unlikely explain the observed $\delta^{234}U$ variability between the years 1780 - 1850. Together, these observations imply that the $\delta^{234}U$ 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.

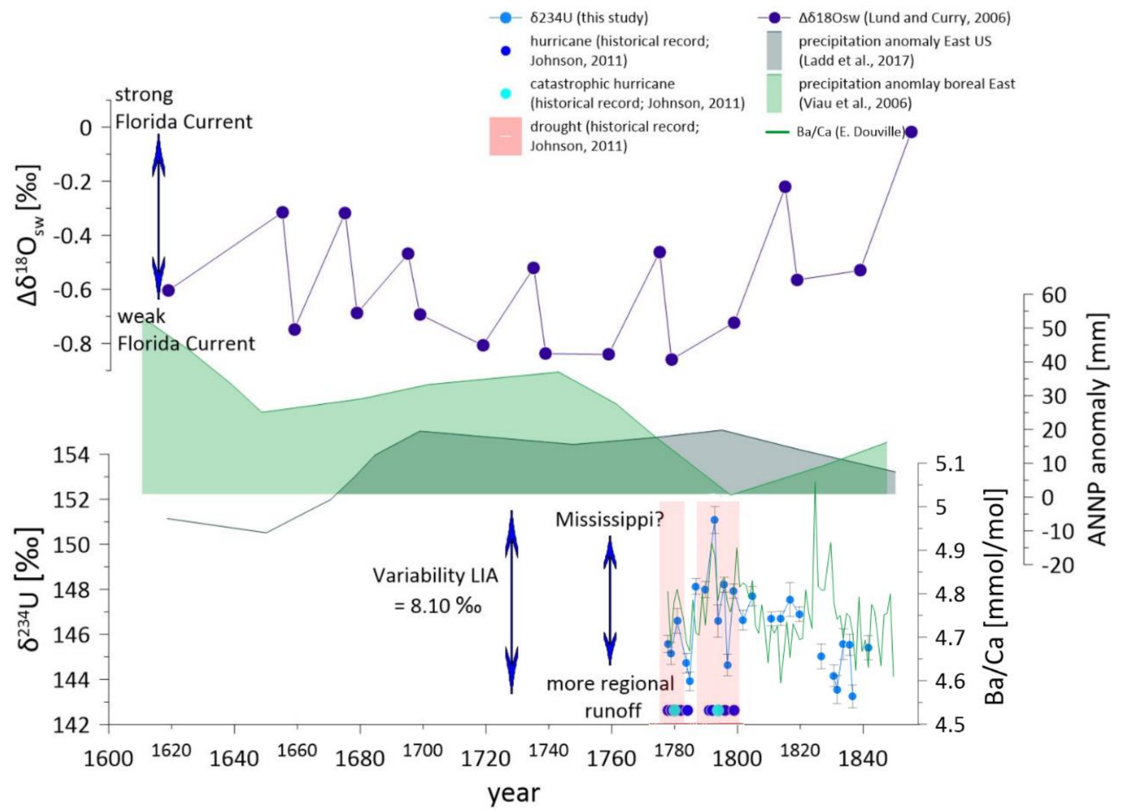

Figure 5: δ^{234}U values (blue) from 1778–1850 plotted together with the timing of hydrological events documented in historical records (Johnson, 2011), indicating times of high hydrological fluctuation with droughts (red), hurricanes (dark blue), and catastrophic hurricanes (light blue). The green line shows Ba/Ca ratios of the coral core corresponding to the δ^{234}U values. During these times, the δ^{234}U values exhibited high variability, ranging from 143.40 ‰ to 151.50 ‰ in 1792. According to the present age model this high value occurred during a period of recurrent major hurricanes. Florida Current strength is inferred from Δδ^{18}O$_{sw}$ 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 δ^{234}U values."

Regarding the late 20th-century interval, we note that the observed δ^{234}U increase is not statistically significant and is therefore not discussed any further. We have clarified this point in the revised text.

To directly address the reviewer's suggestion, we note that a coral core from a site closer to the Mississippi River plume has already been requested. A comparison of this record with the Cuban δ^{234}U time series including Ba/Ca and other potential tracers of Mississippi runoff will be critical for disentangling regional versus distal controls and is planned as part of future work.

Reviewer 1 comment:

I would love to see this record published, but with more geochemical backing of the potential processes modulating the ∂^{234}U variability.

Response:

We sincerely thank the reviewer for this encouraging conclusion. While we acknowledge that further geochemical constraints would strengthen process-based interpretations, we believe that the present study provides a necessary and robust first step by documenting and validating $\delta^{234}U$ variability in a coral archive and by framing the key hypotheses to be tested in future work. We will revise the manuscript to more clearly communicate the exploratory nature of our interpretations and to transparently discuss current limitations.

Reviewer 2 comment:

This manuscript presents a high-resolution annual δ234U record from a Cuban coral covering the past 237 years, with particular focus on the end of the Little Ice Age. I find the dataset valuable and timely. Records from this time interval provide a rare opportunity to explore the short- to decadal-scale behavior of seawater δ234U and its coupling to hydrological variability. The study offers an interesting perspective on how coral δ234U may respond to both local and advected freshwater sources, and it potentially broadens our understanding of the variability of δ234U within the modern oceanic range. In that sense, I consider this work promising and worth publishing after clarification of several issues.

My first concern relates to the definition of δ234U and the role of HU-1. The manuscript states that measurements were bracketed to HU-1 and that HU-1 was treated as secular equilibrium. The authors then re-normalized the δ234U values to another reference. This workflow is confusing to me. If HU-1 is primarily used for instrumental drift correction and mass bias normalization, there is no need to assume that it represents secular equilibrium in a physical sense. For instrumental purposes, it would be sufficient to fix a reference 234U/238U ratio and normalize all measurements relative to that value.

At the same time, δ234U is calculated using specific decay constants, which places the data on an activity-based scale (in the present manuscript the authors adopt the values from Cheng et al., 2013). It is therefore unclear whether the reported δ234U values are intended as purely relative values referenced to HU-1, or as absolute activity deviations tied to the adopted decay constants. In fact, the results of Cheng et al. (2013) suggest that HU-1 is not strictly at secular equilibrium. These approaches are conceptually different, and I think the manuscript should explain more clearly how they are reconciled.

Response:

We thank the reviewer for pointing out that the description of the normalization procedure was not sufficiently clear.

In our workflow, HU-1 was used exclusively as an instrumental bracketing standard to correct for mass bias and drift. For this purpose, its measured $^{234}U/^{238}U$ ratio was fixed to a constant value during data reduction. This step does not require HU-1 to represent secular equilibrium in a physical sense, but only serves as an internal reference ratio.

After instrumental correction, $\delta^{234}U$ values were calculated using the decay constants of Cheng et al. (2013), thereby placing the data on an activity-based scale.

We will clarify this distinction in the revised manuscript.

“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 $^{234}U/^{238}U$ 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. $\delta^{234}U$ was calculated via the processed activity ratio of $^{234}U/^{238}U$ and is expressed in per mil (‰) using the following equation (1).”

Reviewer 2 comment:

The second issue concerns the calibrated δ234U value of CRM112A. After correction, the manuscript reports −38.1 ± 0.3‰. In Figure 2 the error bars appear much smaller (closer to ±0.1‰). My assumption is that the manuscript reports 2σM for its own measurements (?) whereas some of the literature values shown in the same figure (e.g., Cheng et al., 2013) likely report 2σ uncertainties. If different uncertainty definitions (2σ vs. 2σM) are plotted together without being clearly distinguished, this could easily create a misleading visual comparison and should be clarified explicitly. Also, looking at Figure 2 as presented, the reported value appears to only just overlap with Cheng et al. (2013) at the edge of uncertainty, and it does not overlap at all with Pourmand et al (2014) (I think the error presented is also not correct). More recent high-precision work from the same research lineage as Cheng et al. (2013), namely Hu et al. (2025), reports a value closer to −38.49 ± 0.09‰. Compared to that, the value presented here appears slightly less negative. I wonder whether there are any possible reasons that could explain these less negative values, such as measurement corrections or normalization procedures. Although this difference is small and does not affect the discussion of the 1–3‰ variability in the coral record, it does raise questions about absolute accuracy of the methodology. In addition, since δ234U depends directly on the adopted decay constants, I would also suggest that the authors consider recalculating their data using the most recent half-life values (Hu et al., 2025) to ensure full comparability with current high-precision studies. A clearer explanation of the uncertainty definitions, the normalization procedure, and the adopted decay constants would strengthen confidence in the analytical scale used in this study.

Response:

We thank the reviewer for this careful and constructive comment.

We have revised Figure 2 to ensure a consistent and transparent presentation of uncertainties. The lowered CRM 112A results from a mistaken $^{235}U/^{238}U$ ratio for this reference material. When applying the correct $^{235}U/^{238}U$ reference value we obtain -38.5±0.3 ‰ for the 16 values. All values, including our own data and literature values, are now plotted using 2σ uncertainties. The previously shown smaller error bars reflected $2\sigma_M$ (standard error of the mean), whereas the manuscript value of −38.5 ± 0.3‰ refers to external reproducibility expressed as 2σ. This distinction is now clarified in the text and figure caption.

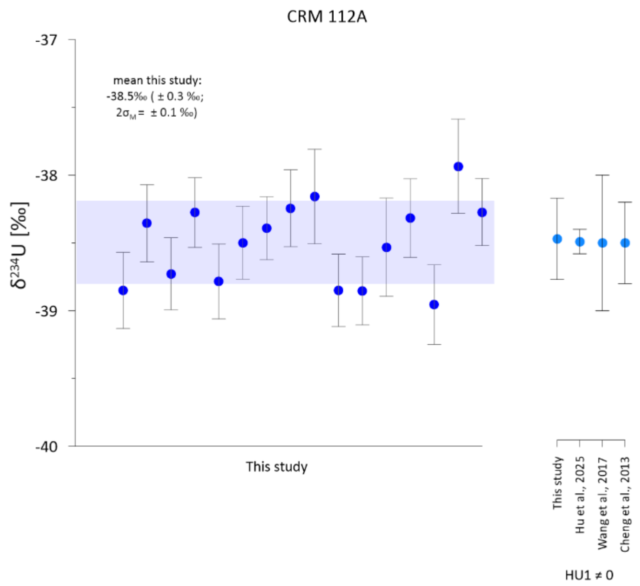

Figure 2: The CRM112A standard was repeatedly measured via the bracketing method with the HU-1 standard.The mean value of −38.5 ‰ ± 0.29 ‰ is in line with other studies (Cheng et al., 2013; Wang et al., 2017; Hu et al., 2025).

In addition, we have included the recently published high-precision value of Hu et al. (2025) in the updated figure. The reported value of −38.49 ± 0.09‰ is now shown for direct comparison. The most recent half-life values are not applied here as the value remains the same as reported by Cheng et al., 2013. We will add a sentence to clarify our choice.

We thank the reviewer for pointing at this deviation, which made us search and find our calculation error.

Reviewer 2 comment:

Finally, while the discussion of Little Ice Age variability is thoughtful and physically plausible, it remains largely interpretative rather than tightly constrained. The manuscript presents several reasonable mechanisms to explain the enhanced variability during 1778–1846, including extreme local runoff events, Mississippi River input enriched in 234U, changes in Loop Current dynamics, reduced Florida Strait throughflow, and land-use changes affecting terrestrial uranium flux. Each of these mechanisms is plausible, and the overall narrative is coherent. However, I do not see any independent constraints that allow one mechanism to be clearly favored over the others. The interpretation therefore remains a set of competing but largely untested hypotheses. Given the availability of other high-resolution LIA hydroclimate records in the Caribbean and Gulf of Mexico, a more systematic comparison or a clearer prioritization of one dominant process would strengthen the conclusions. At present, the manuscript convincingly demonstrates increased δ234U variability during the end of the LIA, but it does not yet identify the primary controlling mechanism with sufficient certainty.

Response:

We thank the reviewer for this constructive comment, which was also pointed-out in review one. We are fully aware that a single coral record from Cuba does not allow for a conclusive interpretation of $\delta^{234}U$ with respect to several possible mechanisms, in particular since such annual variations have not been recorded before. We work on this matter presently in a new and far more expanded project in which we search material to allow assessing the spatio-temporal variance of $\delta^{234}U$ in the Gulf of Mexico. We agree that the original discussion did not sufficiently prioritize among the proposed mechanisms. In the revised manuscript, we will substantially expanded the Discussion to include a more systematic evaluation of the competing hypotheses and we will highlight that the system switches from distal influences during the LIA to more local influences with less variance during the more recent decades. The complexity arose in part from the fact that we were not aware of the deforestation of Cuba in early 18th when we selected our sample. Since this local event coincides with the end of the LIA the interpretation remained ambiguous. Thanks to the use of Ba/Ca we have now a more solid constraint on the initially thought of distal provenance of the signal during the LIA and we greatly acknowledge the helpful comments, which made this aspect much clearer.

"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 $\delta^{234}U$ 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 $\delta^{234}U$ record and the Cuban stalagmite $\delta^{18}O$ 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 $\delta^{234}U$ values observed during this interval."

To further clarify this interpretation, we will add a brief paragraph outlining how future spatially resolved $\delta^{234}U$ records (e.g., from Flower Garden Banks) could quantitatively test the predicted fluvial gradient and refine source partitioning.

"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 $\delta^{234}U$ values without the presence of a high-$\delta^{234}U$ 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 $\delta^{234}U$ in the coral record. Taken together, the available constraints are most consistent with enhanced Mississippi discharge as a principal contributor to the late LIA $\delta^{234}U$ 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 $\delta^{234}U$ 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."

We believe these revisions address the reviewer's concern by moving from a set of plausible mechanisms toward a more clearly constrained and hierarchically structured interpretation.

Reviewer 2 comment:

Overall, this is a promising contribution that provides a valuable new dataset. Addressing the issues above would significantly strengthen the manuscript and enhance its impact.

Response:

We thank the reviewer for this positive assessment and for the constructive suggestions. We have addressed the points raised above and believe the revisions have significantly strengthened the manuscript.