

Geochronology Discuss., author comment AC2
<https://doi.org/10.5194/gchron-2022-10-AC2>, 2022
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Reply on RC2

Paul Töchterle et al.

Author comment on "²³⁰Th/²³²Th isochron dating of cryogenic cave carbonates" by Paul Töchterle et al., Geochronology Discuss., <https://doi.org/10.5194/gchron-2022-10-AC2>, 2022

We want to cordially thank Dr. David Richards for taking the time to provide these very helpful comments. Our response in detail:

- [...] *For consideration.*
Line 39. "In nature, values for (230Th/232Th)₀ vary by orders of magnitude". Please expand on this to report on the sources (and partitioning) of common and radiogenic 230Th, dissolved, detrital and colloidal.

We will add a sentence on different sources and phases of Thorium after this line.

- *Line 109: BCE is equivalent to BC.. you can't redefine the zero point or datum CE. Use of BP where present is defined as 1950 CE is preferred.*

Makes sense. We'll change all ages to BP.

- *Line 114: Please address the burgeoning literature associated with probability density functions, kernel density estimates (with detrital zircons, speleothem ages, 10Be moraines etc.). Can you justify your illustration of the statistical distribution? I appreciate that your pdfs are the result of a sensitivity analysis, but they may over-emphasize the relative frequencies.*

This is a very good point but addressing it needs a bit of discussion:

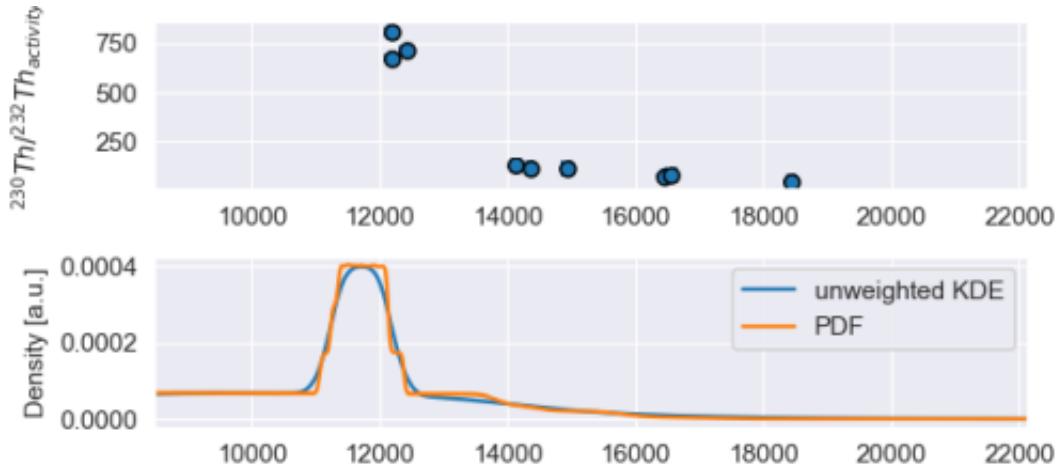
Our intention with the PDFs was mainly to **visualise the possible range of corrected ages**, based on "reasonable" (²³⁰Th/²³²Th)₀ correction factors for the presented cave setting. We appreciate that KDEs are now preferred in many fields of geochronology (OSL, fission track, etc.), so it should be explained why we do not use them here:

From our understanding of the literature, the bandwidth of KDEs is determined as a function of the overall distribution of central values (e.g. using the Silverman [1] or Scott [2] method), but not the analytical uncertainty of individual measurements. To incorporate uncertainty, there is the possibility to apply monte-carlo based subsampling and choose a user-defined bandwidth [3], but this approach is more suitable for larger data sets, computationally expensive and not well established yet. For our intents, we thought it would be more appropriate to use PDFs since they allow us to directly control the width of the distribution, which mainly depends on the uncertainty of the

$(^{230}\text{Th}/^{232}\text{Th})_0$ correction factor, keeping in mind that Gaussian distributions are an assumption for U/Th ages to begin with.

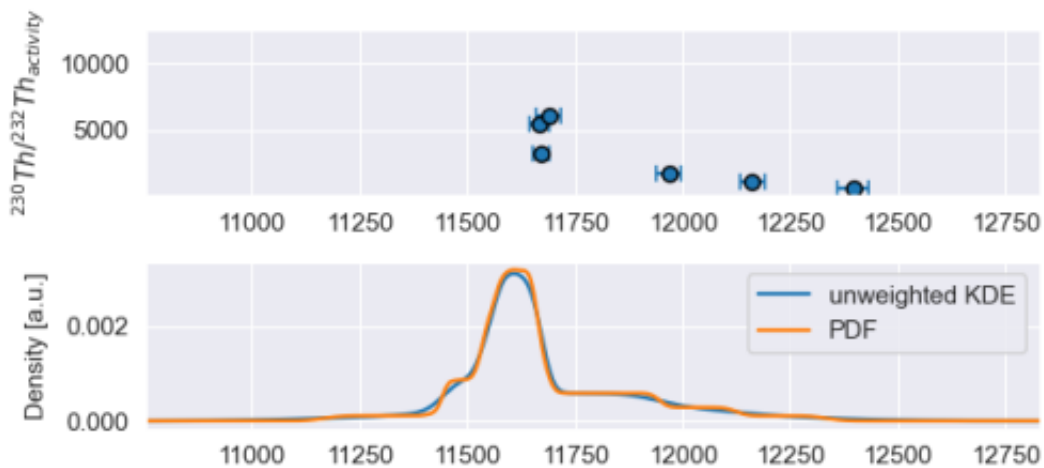
For patches 1 and 2, both methods (KDE and PDF) essentially yield the same result, as shown in the figures below:

Patch 1:



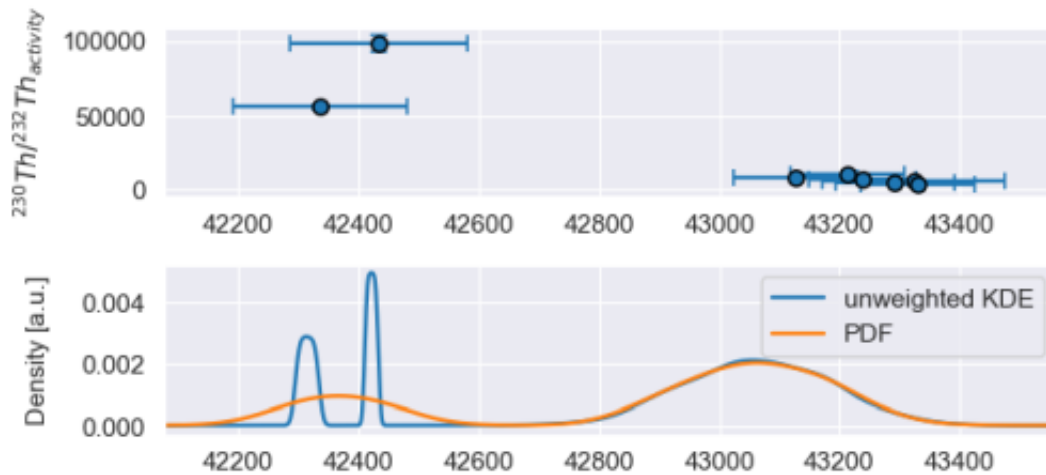
upper panel - uncorrected age in years BP vs measured $^{230}\text{Th}/^{232}\text{Th}$ activity ratio; lower panel - KDE and PDF of corrected ages

Patch 2:



However, for patch 3, the KDE produces an unrealistic bimodal distribution for the very 'clean' age cluster at $\sim 42,300$ BP. Because of the very low initial ^{230}Th , central values of the corrected age ensemble clusters tightly, but the analytical uncertainty of the measurement is not accounted for. PDFs do not have this issue.

Patch 3:



This is the main reason why we chose PDFs over KDEs. We felt this discussion would be distracting to readers and is not essential to the main focus points of the paper: Constructing isochrons is important when dealing with sub-optimal sample material. We are reluctant to add these considerations at length, because we believe it will be distracting to the readers and – as we show above – is of little relevance for this study. We are considering adding a sentence to the respective Method part, stating that “we chose PDFs over KDEs because the former consider the analytical uncertainty directly”.

- [1] B.W. Silverman, “Density Estimation for Statistics and Data Analysis”, Vol. 26, Monographs on Statistics and Applied Probability, Chapman and Hall, London, 1986.
- [2] D.W. Scott, “Multivariate Density Estimation: Theory, Practice, and Visualization”, John Wiley & Sons, New York, Chichester, 1992.
- [3] Weij, R.; Woodhead, J.; Hellstrom, J.; Sniderman, K. An exploration of the utility of speleothem age distributions for palaeoclimate assessment. *Quaternary Geochronology* 2020, 60, 101112, doi:10.1016/j.quageo.2020.101112.

- *Line 129: Provide evidence for the composition of the CCC, i.e. calcite.*

This was also criticised by reviewer 1 and we will remove this statement for lack of a comprehensive dataset to support the statement.

- *Line 174: Rephrase this statement.. a concentration cannot be expressed as a ratio.*

Agreed.

- *And on this front, please reflect on the use of other indices for detrital components, Al, Zn, Ti etc.. Perhaps future studies could investigate trace elemental variation more fully.*

Indeed, we did not consider using, for example Al, as a proxy for detrital contaminants. This could be a promising approach and we will add a sentence to the implications part to promote it.

- *Line 176. “grouped and sorted ... on a visual basis”. Maybe better to say “visually grouped on the basis of relative surface area and roughness”. Expand. What does roughness mean here? “Relative surface area” – per unit volume? Types A, B and C – list here and refer to Supplementary images.*

We will rephrase this part and drop “roughness” because it is redundant.

- *Fig. 4. Why is the 95%CI not 'symmetrical' w.r.t. the regression line? Or do these shaded areas correspond to the confidence intervals for the global data set for each patch, which is then overlain with regressions for subsets.*

We used the seaborn package for Python 3 for these plots, which is a standard tool. The documentation of the linear regression function states that the depicted confidence interval is generated from multiple regression lines of a bootstrapped dataset – hence the asymmetry.

<https://seaborn.pydata.org/generated/seaborn.regplot.html>

- *Also, your isochron analysis is based on 3-D methods as described in Ludwig and Titterton (1994). Please guide the reader to the tools you have used - Isoplot/Ex, IsoplotR or alternative? How have you approached error correlations?*

We used our own python script, which used the same regression models as IsoplotR. We will add this information at an appropriate location in the text.

Regarding error correlations, we used the least squares method to calculate the regression lines (see line 115). This algorithm does not require error correlations (ρ parameter in IsoplotR), which are only necessary to calculate maximum likelihood regression.

- *Line 184. This is the first mention of $(^{230}\text{Th}/^{232}\text{Th})_t$ - this should be defined earlier. Is this at time $T = t$, i.e. time (age) since precipitation $T=0$, and also referred by others as measured value (m).*

The $(^{230}\text{Th}/^{232}\text{Th})_t$ terminology is introduced in line 38. We will change this introduction line to make it more prominent and thorough.

- *Line 209. The data point with most leverage is not an age, it is a data point in isotope space.*

Agreed. We will rephrase it.

- *Table 1. Some uncertainties = 0 in the $(^{230}\text{Th}/^{232}\text{Th})_t$ column. Please correct.*

Good catch. We will correct it.

- *BCE – please correct. Use age* and define the datum in *footnotes. BCE ≠ years before 1950.*

Will change this.

- *Placement of the isochron age derivation in the final column is ambiguous – is this all data for each patch of subset?*

As described in the main text, these are the values of the respective subset. We will change the placement for patch 2 to better represent this.

- *What does isochron-corrected age mean? I presume this is age after correction using derived initial Th for this patch. Please add more detail in footnote. Or remove this column because it is awkward to define these as single ages when they are not independent of the other analyses for the specific patch.*

Agreed, we will delete this column.

- *Line 266. The initial Th ratios calculated do not 'theoretically' represent the values of the 'residual water' from which the CCC precipitated. The water will have more than one source of Th (dissolved, particulate, adsorbed, complexed) and the partitioning between the liquid and solid phase will be complex and variable. The initial Th ratios are representative of the components adsorbed or coprecipitated.*

Agreed. This part will be rephrased.