

Geochronology Discuss., author comment AC1
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Reply on RC1

Paul Töchterle et al.

Author comment on "²³⁰Th/²³⁴U isochron dating of cryogenic cave carbonates" by Paul Töchterle et al., Geochronology Discuss., <https://doi.org/10.5194/gchron-2022-10-AC1>, 2022

Firstly, we would like to thank Karel Žák for taking the time to provide us with this very helpful feedback – it is greatly appreciated. Below is our response to the review comments in detail:

- *General Comments:*

One of assumptions on which is based this study is formation of all CCC particles in one patch within one water freezing event. The reasoning for this assumption is based on the occurrence of typical sequence of CCC morphological types, each characterized by carbon and oxygen stable isotope data in an explainable logical sequence, which is in accord with known principles of stable isotope fractionation under water freezing conditions. This assumption is most probably valid, nevertheless, certain uncertainty remains. Under oscillating climate of the Last Glacial similar climatic conditions could occur repeatedly and all other factors are constant or highly similar – cavity morphology, its depth below the surface, lithology and chemistry of the limestone, characteristics of the epikarst zone, etc. We can therefore speculate that repeated freezing conditions with similar morphology of the ice fill the cave and similar chemistry of water which freezes could produce repeatedly the same sequence of morphological types with similar evolution of C and O stable isotope data in the carbonate. After ice melting the products of two or more freezing events could have been deposited together in one patch. An approach which can possibly shed some light on this can be detailed mapping of size distribution and distribution of individual CCC morphological types within each of studied patches together with detailed mapping of patches (giving their dimensions and shapes).

We absolutely agree that similar CCC-forming conditions could have occurred repeatedly at a given site and produced similar CCC morphologies with similar trends in trace element and stable isotope composition. Note that these chemical and physical properties do not change anymore after CCC precipitated and conserve the original composition. The ²³⁸U-²³⁴U-²³⁰Th system we used in this study, however, evolves continually through radioactive decay. It is highly unlikely that CCCs from different precipitation events would – by accident – form a highly correlated isochron. Our results (especially Patches 2 and 3) show that the isochron approach in fact allows us to reliably differentiate multiple formation events. As is stated in line 55, we do not *assume* but *test the hypothesis* that individual CCC particles form within achievable dating precision. To address this comment, we consider rephrasing the statement in line 55 to state more clearly that we do not make an assumption.

- *Since the study site is presented as a CCC locality for the first time in the international literature, the position of the studied sites within the cave should be presented in more detail, either in a cave map (can be included in an electronic supplement) or by coordinates and/or description in the text.*

In accordance with this comment and others that regard the study site, we will add an extended site description to the supplementary material and add a reference to the main text (line 66).

- *I also consider as important to specify in the discussion from which direction the water producing the CCCs most probably entered the cave. Was it dripping water or flowing water from some kind of periodic water stream? This has some consequences regarding the transport of clay particles within the cave and thus for the interpretation of Th contamination of the samples.*

We are afraid there is no way of knowing this with the evidence we have available. In [1], there is some description of a paleo-flow of water towards the north during a phreatic phase as indicated by scallops on the cave walls. However, this phreatic phase unequivocally predates the (vadose) phase when CCCs formed. Besides that, there are no good indicators of where water was flowing. It seems more reasonable to assume that the water was dripping from the ceiling onto pre-existing ice bodies, rather than a stream pooling and freezing, but there is no direct field evidence available. We will point out those aspects in the extended site description we will add them to the supplementary material.

[1] Gunn, J.; Fairchild, I.J.; Moseley, G.E.; Töchterle, P.; Ashley, K.E.; Hellstrom, J.; Edwards, R.L. (2020): Palaeoenvironments in the central White Peak District (Derbyshire, UK): evidence from Water Icicle Close Cavern. *Cave and Karst Science*, 47, 153–168.

- *It would be useful to compare the levels of clastic Th contamination of the studied samples with $^{230}\text{Th}/^{232}\text{Th}$ ratios of other studied and published localities.*

Many authors only published the final ages without providing these additional data. Also, a detailed description of the sample preparation (e.g. cleaning steps and if samples were drilled or digested as a whole) are usually lacking, which makes it difficult to compare these published data. From those papers that did provide $^{230}\text{Th}/^{232}\text{Th}$ ratios, all analyses fall within the range we observed in this study (i.e. $\sim 10 - 10,000$), and often times show large variation of 2-3 orders of magnitudes. We did not mention these studies explicitly, because we do not want to point fingers - but this might indicate that these studies possibly fell into the trap of reporting multiple CCC formation periods because of correcting contaminated samples with a poorly chosen $^{230}\text{Th}/^{232}\text{Th}$ initial ratio. We will cite a selection of reported values for $^{230}\text{Th}/^{232}\text{Th}$ in the discussion part to address this point.

- *Detailed comments*
The studied site - Please give an information here about the cave chimneys directed toward the surface. Are they all sediment or limestone boulder blocked? The cave entrance was artificially excavated? What have possibly been the circumstances of cave connection toward the surface in the Last Glacial?

We will add this information to the extended site description.

- *Results - How do you know it is only the calcite? Based on crystal morphology only? There is no information about XRD mineral identification in the Methods.*

We have XRD data for several specimens, but not for most of the samples of the presented data set. We will remove the respective sentence in line 129 because indeed, we cannot say for sure.

▪ *References*

The list of references is complete and there is no extra reference. The guide for authors is not followed completely. The journal names should be abbreviated and the order of references should follow the guide for authors (copied from this source):

- Single author papers: chronologically, beginning with the oldest. If there is more than one paper in the same year, a letter (a, b, c) is added to the year, both in the in-text citation as well as in the reference list.

- Co-author papers: first alphabetically according to the second author's last name, and then chronologically within each set of co-authors. If there is more than one paper in the same year per set of co-authors, a letter (a, b, c) is added to the year both in the in-text citation as well as in the reference list.

We will change the reference list to chronological ordering and abbreviate all journal titles – thanks for taking the time to also check the reference list!

Comments from the main text (gchron-2022-10-RC1-supplement.pdf):

Line 34: Good point. We'll specify that we're talking about karst water.

Line 36: "speleothem" added

Line 40: An error in the literature database – corrected now.

Line 65: We will add this information to the extended site description of the supplement, but we would like to emphasise that it was our intention to reduce cave-specific aspects and focus on the geochronological methodology.

Line 80: We will add this information to the extended site description.

Figure 2: added VPDB to axis labels

Line 129: see above – will be removed.

Line 199: The abbreviation PDF (probability density function) is introduced in the methods section in line 113.

Line 267: Correct. We will add this information "[...] including all sources of Thorium (such as solutes, colloids and particulate matter)".

Line 289: We'll rephrase "Russian" to "eastern European and Siberian".

Line 301: Actually, both patch 2 and 3 show evidence for at least two freezing events. This is shown by the offset from the regression lines in figure 4. We believe we made this clear in Results and Discussion.

References: see above – will be changed in the revised manuscript