REVIEW #2

"U and Th zonation in apatite observed by synchrotron X–ray fluorescence tomography and implications for the (U–Th)/He system" by Sousa et al. is an interesting and well-written manuscript that details a method to non-destructively visualize, in 3D, patterns of zonation in parent nuclides and zircon inclusions in apatite. The manuscript includes clear, step-by-step instructions with sufficient detail such that this study could be replicated. I believe this manuscript should be published in Geochronology and is valuable to the community. Below I outline some general comments followed by technical corrections and suggestions:

General comments:

The limited access to synchrotron facilities and beamtime seem to be an issue, as explained in Sect. 3.6. It would be helpful to have more details about how you got beamtime, how much it cost, and how long the actual analyses took.

We agree that synchrotron access is important, and will add some detail about the proposal we used to gain access to the facility. For details about the length of time required for analyses, see text section 2.1 and 2.4.

Could this method be modified or expanded upon for labs interested in acquiring data for multiple grains? For example, you have a grain imaged at a resolution of 2µm^2 (Fig. 2 caption), does this significantly decrease the analytical time? Is it possible to mount several grains for analysis at the same time? I know you did not do this in this study, but it would be helpful to know if higher throughput is possible.

We are certainly interested in finding a way to expand access to this type of data, decrease time required, etc, as discussed in section 3.6. Our thinking is very much in line with the type of questions listed here by reviewer #2, as we allude to in section 3.6. At the current stage, the tradeoffs between resolution, speed of analyses, and utility of information are not fully explored, but are of significant interest. We will add some text to section 3.6 better explaining this.

I would like a little more justification for the samples you chose to analyze. Why analyze such small grains that have no demonstrated issues with unexplained overdispersion (that could have been attributed to zonation)? Did you attempt to analyze grains that have complex zonation?

Section 2.2 discusses the criteria we used for choosing the samples measured to date. We agree with the reviewer that future work specifically studying

overdispersed crystals would be worthwhile, and we explicitly suggest this in Section 3.1 of the manuscript. The data shown in this manuscript includes a highly diverse set of types of complex zonation patterns, as shown in figures 1, 2, and 5.

Are there (or could there be) issues with helium loss attributed to heating during analysis?

We do not believe it is likely that x-ray illumination would significantly heat the sample. It will locally dump milliwatts of energy into a line through the sample that is 2um x 2 um extending the length of the sample. Since that power is spread over a line through the sample, it has ample opportunity to dissipate. Future work thermally imaging a crystal during analysis would explicitly answer this question. In the case that sample heating was sufficient to potentially drive He diffusion measurably, that could be fully ameliorated by degassing the grain and measuring He prior to XRF microtomography, rather than after.

A table with sample names, (U-Th)/He ages and references, crystal dimensions, F_T values, and the number of / a brief description of tomographic slices acquired and the resolution would be useful.

We prefer to limit the figures and tables in the paper to those that directly contribute to understanding the new contribution provided by the synchrotron XRF microtomography method. We are explicit in the manuscript that although the thermal histories of these samples are of tectonic importance, they are not the focus of the paper. For these reasons we prefer to leave these details in textual form in the methods section.

L97: Could you include photomicrographs of the analyzed grains? You state that you picked grains with no visible inclusions but in the video supplement for MGB5-2 there appear to be large near-surface inclusions.

We do not have photomicrographs of all of the analyzed grains. The typical photomicrographs are taken primarily to document crystal dimensions, not presence or absence of inclusions, which require subjective interpretation by an individual, with use of crossed polars, ethanol immersion, and a very steady hand to visualize and interpret with certainty. The near surface inclusions visible in the MGB5-2 video are visible in the XRF data because of higher U and Th, but are also shown to be apatite in apatite inclusions as discussed in section 3.2, and would not necessarily be visible in photomicrographs.

L175: Does the dot of epoxy covering the bottom termination of the apatite in the mount influence the signal?

The epoxy will absorb some X-rays, which can be seen in the images, but it is not an important effect for these crystals, as it is relatively low density.

L214-L220: You explain in Section 2.5 how concentrations were acquired and the uncertainties on them, but it is distracting that there is no ppm value attached to the color scale in Figure 2. I suggest referring the reader to the discussion in Sect 2.5 in the figure caption.

We thank reviewer #2 for this suggestion, and will add the suggested reference to the figure 2 caption.

L214-L220: Are there relevant citations for, or could you expand upon, how you arrived at the uncertainties on the concentrations? Are these grains degassed/dissolved yet? It would be nice to see if the "reasonable" abundances are actually in line with the actual abundances measured by ICP-MS.

The concentration data shown are directly calculated from the XRF microtomography results, as explained in section 2.5. The individual crystals imaged are neither degassed nor dissolved yet. The absolute abundances from XRF are dominated by systematic errors from incomplete modeling of the solid angle and total efficiency of the XRF detector and will be factors of 2 to 5. We encourage reading the values as order of magnitudes. For MGB5 there are published aliquot average U and Th concentrations for the aliquots reported in Mcaleer (2009), the range of which is fairly consistent with the concentrations derived from the XRF tomography and shown in Figure 1 and 5. However, we have not discussed this in the manuscript because we are explicitly not representing the XRF data as a useful absolute U and Th concentration measure (just order of magnitude).

L240: In Table 1, for the definition of a labelmap, how are voxels that delineate the exterior of the grain classified?

We explain the process of delineating the exterior of the grain immediately below Table 1 in the text of section 2.6.

L245: I would like to see a brief discussion of what other elements (major? minor? trace?) can be visualized with this method. Subsequently, why did you choose to map Sr (and Y?) as a proxy for crystal volume rather than P?

The XRF spectra and abundance analysis shows clear presence (and maps) for elemental maps for P, Ca, Mn, Fe, Sr, Y, La, Ce, Nd, W, Th, and U. There is some evidence of Cu and Zn.

While P, Ca, Mn, La, Ce, and Nd are visible, these are significantly attenuated (3 orders of magnitude) due to self-absorption by the sample and estimates of abundances would be very uncertain. We discuss this in the text of section 2.5 for Ca attenuation. Sr and Y both give very strong peaks, and are X-ray fluorescence energies that are both high enough to not be severely attenuated by self-absorption, and also near to the energies of Th, and U.

We have example XRF spectra with labelled peaks that can be included in an appendix if necessary.

L297: You emphasize the value of the stopping distance several times throughout the manuscript but then round them. I understand why you have to do this. Do you expect that this has any appreciable impact on the calculated F_T values? Do you expect the resolution of the mapped zonation (e.g., $1\mu m^2$ vs. $2\mu m^2$ vs. $10\mu m^2$) to have an impact on the calculated F_T value?

We do not expect the rounding to have an appreciable impact on the calculated Ft values. Because of the high spatial resolution, the relative percent of total alphas that fall into a rounded voxel is low. Furthermore, since we round to the nearest integer, some will be rounded into the crystal, and some rounded out of the crystal, which would act to minimize any bias, so long as there is a roughly symmetrical distribution of percent of each rounded voxel inside vs outside the crystal. Decreasing the resolution of the measurements would certainly make this more of a problem, but the extent to which that would be an issue is not constrained here because we are only presenting data at the higher 1um3 resolution.

L374: For illustrative purposes you calculate an F_T value for a 50 Ma uncorrected age—this sample has a published mean helium date of 5.90 ± 0.42 Ma. Why the discrepancy? Additionally, the small size of the grain is going to have a large impact on the calculated F_T. Would it be possible to recalculate these data for a more typically sized grain?

We explicitly use an example age that is highly deviated from the actual published ages to avoid any confusion that the example ages in table 2 are actually calculated ages (they are not calculated ages, just examples to show how the differences in Ft would lead to different corrected ages). The exciting new contribution here is the fact that we can directly calucate FT values based on the actual measured U Th distributions (not assuming anything about zonation).

Recalculating these data for a larger grain would require an assumption about zonation, and so we do not do so.

L374: In Table 2, can the "Qt_Ft" method be additionally labeled as "traditional" or "geometric"? Does the Qt_Ft method use the Ketcham et al., 2011 equations for calculating F_T?

We thank reviewer #2 for requesting clarification. We will add some text to the table to clarify that the QTFT method uses crystal dimensions derived from synchroton data (just length and width). QT FT does use Ketcham 2011 alpha stopping distances, as explained in the citations for QT FT.

Technical corrections/suggestions:

- Add a line to the abstract that briefly describes the samples.

  The samples are described in section 2.1, and the details of the specific samples do not bear on the fundamental contribution of this paper which is the focus of the abstract. Further, there is no reason to expect that this method wouldn't work on any apatites, and so including the details of the samples in the abstract would require clarification that goes beyond the brevity and focus we are trying to accomplish in the abstract.

- Where there are multiple citations prefaced by 'e.g.,' or other words, there are extra parentheses (for example, L27, L29, L36, L50, etc.)

  We thank the reviewer for this comment, and will make sure such typographical issues are fixed for publication.

- L35: the listed stopping distances for apatite in Ketcham et al. (2011) are 5.93-22.25μm but you have 13-34μm listed?

  We thank the reviewer for pointing this out. 13-34 um is the total range of all decay stopping distances for the three U and Th decay chains from Farley et al 1996, and 5.93-22.25 is the range of mean stopping distances for the three chains AND samarium from Ketcham. To avoid confusion we cite both papers and just list the rough average stopping distance of 20 um.

- Adding a discrete color scale next to figure 2F would be helpful rather than explaining the color scale at the end of the figure caption.

The three end member RGB map of 2F does not lend itself to visual color scale like the linear scale of the other frames, so we describe the three end members in the figure caption instead.

- L222, L224: Gürsoy should have an umlaut.

- **We thank the reviewer for catching this, and will fix it.**

- L372: FT should be F_T.

We thank the reviewer for catching this, and will fix it.

- Consider citing Zeigler et al., 2023 (https://gchron.copernicus.org/articles/5/197/2023/) where discussing updates to F_T calculations.

We thank the reviewer for suggesting this citation, and will add it.