REVIEW #3

"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.

I will preface this review by making it clear that my expertise lies not in geochronology but in experimental physics, in particular synchrotron-based data acquisition and analysis, with significant experience in XRF mapping. I therefore limit my review to the synchrotron methods and analysis.

This paper aims to increase the accuracy of (U-Th)/He thermochronology by accurately mapping U and Th zonation in apatite crystals using X-ray fluorescence tomography. The improvement in accuracy hinges on accurately measuring the U and Th concentrations throughout the apatite crystals. Table 2 suggests that this method increases accuracy over traditional methods by ca. 10%, and by ca. 7% over assuming homogenous elemental distributions.

However, I find a major flaw with this method:

"Importantly, this analysis does not account for attenuation of the X–ray fluorescence by the sample itself. This attenuation varies systematically with the energy of the main fluorescence line. Because the X–ray path through the sample to the detector varies for each x and w value, trying to account for this effect accurately would be difficult and error prone."

We disagree with reviewer #3 regarding the interpretation that our treatment of attenuation by the sample is a major flaw with the study. In particular, this seems most likely related to the reviewers stated non-expertise in the details of the geochronology application, which is our primary focus. In particular, the biggest new contribution here is the high fidelity mapping of the relative distribution of U and Th spatially throughout a crystal. This is not significantly effected by self absorption. The uncertainties on absolute abundance estimates is openly discussed in the manuscript and does not have a negative impact on the geochronology application here.

Additionally, we have done a self absorption correction and have these results available to add to an appendix if necessary. Results show that the correction for Ca is significant but not overwhelming. The correction for the concentration of Th, U, Sr, and Y in the MGB5-2 grain are all minimal.

The attenuation of the X–ray fluorescence by the sample itself, known as self-absorption, is significant. For example, for U fluorescence (16.366keV) the attenuation length (where 1/e of the initial intensity remains) is ca. 260 um, while for Th fluorescence (12.252keV) the attenuation length is ca. 130 um (https://henke.lbl.gov/optical_constants/atten2.html). For sample MGB5–2 (diameter < 100um) this may not be an issue, however, for 03PH307A- 2 and AP-1 with diameters more than 200um this will be significant and cannot be ignored.

The X-ray path for 03PH307A- 2 was about 60 microns.   The crystal was oriented so that the shorter axis was the path taken by the X-rays to the detector.

As the reviewer may know, "attenuation length" means the intensity has dropped by 1/e (to 37% of the initial intensity).   The attenuation length for Th La1 (which is 12.97 keV) is 140 microns. The attenuation length for U La1 is 160 microns.   Th La1 X-rays from the far side of the grain (60 microns) will be attenuated to 66% of the initial intensity. U La1 X-rays from the far side of the grain will be attenuated to 69% of the original intensity.   That is the worst case here: the average depth is only 30 microns (so 80% and 83% of the initial intensity for Th and U, respectively).   One can conclude that XRF analysis without correcting for self-absorption will result in Th/U ratios that are systematically high by up to 5%.

We are claiming that absolute abundances are "better than order-of-magnitude" levels but could easily be off by factors of 2. The relative abundances (say the Th-U ratio) should be much better than that, though we are not claiming that they are correct to 2 significant digits.

The concerns of the reviewer here do not have a significant implication for the primary results of this study (the 3D imaging of U and Th relative abundance in apatite crystals). It seems most likely that the reviewer is mistakenly interpreting the large uncertainties on absolute abundance measurements (which we openly and explicitly address in the manuscript) as a flaw in the study, which it is not.

The error introduced from not accounting for self-absorption would be significant, and likely exceed the claimed benefits. Indeed, correcting for this is difficult, but solutions to this problem exist, for example:

1. Zichao Wendy Di, Si Chen, Young Pyo Hong, Chris Jacobsen, Sven Leyffer, and Stefan M. Wild, "Joint reconstruction of x-ray fluorescence and transmission tomography," Opt. Express25, 13107-13124 (2017)

2. Yang, Q., Deng, B., Du, G., Xie, H., Zhou, G., Xiao, T. and Xu, H., Q. Yang*et al.*. X-Ray Spectrom., 43: 278-285 (2014)

3. Gao, J. Aelterman, B. Laforce, L. Van Hoorebeke, L. Vincze and M. Boone, "Self-Absorption Correction in X-Ray Fluorescence- Computed Tomography With Deep Convolutional Neural Network," inIEEE Transactions on Nuclear Science, vol. 68, no. 6, pp. 1194-1206, (2021).

Additional comments.

1. How long does each tomography slice take to acquire? How many could you collect in 1 day of beamtime?

This would vary significantly depending on crystal size and choice of tomography parameters (corresponding to spatial resolution). For the data presented in this paper, we collected roughly 1 full crystal of tomography data per 1 day of beam time. We agree that this is useful information to include and will add it to the manuscript. With upgrades to X-ray facilities and detection electronics, the beamline will probably be able to go between 2 to 5 times faster without degrading data quality.

2. Is there an application to a lab source? What would need to happen to be able to apply this to a lab?

If this refers to collecting such data using a laboratory X-ray source, that seems unlikely. This work used a micro-focused X-ray beam with very high flux: the focus beam size will determine the ultimate pixel size and the flux was on the scale of 10^{12} monochromatic photons/sec.   It would probably be feasible on a micro-focused bending magnet beamline with 1000x lower brightness, but probably be considerably slower to achieve similar data quality or have a much lower count rate that would make U distribution a bit more difficult to see in a reasonable amount of time.

3. Using self-absorption corrections, what is the viable upper limit of sample size?

This would depend on the density and elements to be analyzed. For apatites, 200 microns would certainly be correctable, and 500 microns might be possible – Ca might be uncorrectable, but Th, U, Sr, Y probably would be correctable.   For biological samples (density below 2, mostly water and carbon), samples as large as 1 mm are feasible.   We note, however, that data collection for a given spatial resolution would go as the square of the size of the object. That is, a grain 200 microns across would take 10x as many data points to get the same spatial resolution as a grain that is 60 microns across.

4. Can the homogenous approximation be estimated with a simple 2D fluorescence scan? In this case the is there an upper size limit to the measurement? This seems like a possible way to achieve a measurable improvement with significantly fewer experimental complexities.

It is unclear what reviewer #3 is referring to by "homogeneous approximation" here.   One can do 2-D XRF mapping. For grains such as those analyzed here, quantification of XRF spectra to get abundance would be complicated by the non-uniform sample depth. Making a thin section to give a uniform thickness (say, 30 microns) would be the standard analytic approach in that case.