## Florian Hofmann (Referee)

Referee comment on "U and Th content in magnetite and Al-spinel obtained by wet chemistry and laser ablation methods: implication for (U-Th)/He thermochronometer" by Marianna Corre et al., EGUsphere, <u>https://doi.org/10.5194/egusphere-2022-520-RC1</u>, 2022

This manuscript explores the measurement of U and Th in magnetite and spinel samples to assess the expected uncertainties with modern analytical techniques at different concentration levels. Magnetite and spinel tend to contain low concentrations of U and Th, which makes it difficult to use them for geochronology, but the ubiquity of magnetite and spinel, and the relatively high closure temperate of helium make them interesting target phases. This manuscript presents useful guidance on how to optimize measurements and outlines the limitations of modern analytical techniques. It represents a significant step towards exploring the potential of magnetite and spinel (U-Th)/He dating and making it possible to use these techniques routinely.

Dear Florian Hofmann, thank you for your interest and we appreciated your constructive and helpful suggestions. Please find below the answers to the different points that you raised.

In my opinion, this manuscript is well-written, and the data is presented effectively, but it could benefit from minor revisions, as outlined below. The topic fits within the scope of Geochronology, but I would suggest changing the article type to "Technical Note" since it fits the description of that category more than that of a "Research article".

As we do not clearly propose an analytical protocol but rather discuss how dispersion in U-Th measurements arises and fluctuates for the two analytical methods (wet chemistry and LA-ICP-MS), we do not believe that this manuscript can be considered as a true "Technical Note".

I agree with the comments by RC1, and I will only mention additional points below:

Line 42: Change "fault" to "faulting".

Thank you, we will correct this sentence in the next version of the manuscript.

Line 45: Change "radiogenic" to "radioactive".

Ok, we will correct tit.

Line 46: Change "neighbor" to "neighboring".

## Yes, we will correct it.

Line 56: The quoted number of "0.0012%" is incorrect; 0.0012 is the fraction (not percentage) of the contribution of Sm to the effective U concentration (eU), which equates

to 0.12%. The exact contribution of Sm to the radiogenic budget depends on the sample dependent U/Sm and Th/Sm ratios. I have seen some samples with low U and Th concentrations and relatively high Sm concentrations in which Sm did contribute to the total amount of 4He to a level above that of the measurement uncertainty. For most samples, the contribution of Sm to the measured amount of 4He is negligible, but can't be ruled out a priori. I agree with not discussing Sm in the manuscript, but the reasons should be clarified. Thank you, we will correct this error in the next version of the manuscript. We did not work on Sm because the used spikes were not adapted in term of <sup>149</sup>Sm content, but we agree that Sm should be measured routinely.

Table 1: Pictures of the samples in addition to the descriptions would be helpful

We agree and we will add photos of each sample before crushing.

Line 93: Was the goethite removed before analyzing the magnetite?

No, we did not manage to design a goethite separation protocol from magnetite.

*Were U and Th partitioned between the magnetite and goethite?* 

It is an interesting question, but we do not know precisely the answer. The step-by-step pH decrease experiments presented in Appendix A, suggest that U (and Th) is not adsorbed onto the magnetite / goethite surface. Only synchrotron XANES experiments will allow to address this question and to determine the actual speciation and location of U and Th atoms. Our goal here was to synthesize a product having a composition/crystal-structure the closest to that of magnetite. The standardization results with this product are actually very promising.

Please discuss this possibility and mention any data you might have.

In addition to the fact that we lack relevant data to discuss this issue, owing to the good results obtained with our synthetic standard, discussing the U-Th partitioning between goethite and magnetite seems slightly out of scope.

Line 100: Why were the samples ground into a powder?

We finely powdered the (natural) samples to have homogeneous, and thus identical, samples for both wet chemistry and laser ablation analysis. We will add additional information about the purpose of grinding the samples in the next version.

The stated goal is to assess uncertainties as a result of single-aliquot dating of magnetite grains, but this process homogenizes the sample similarly to a two-aliquot approach. As a result, all intra-sample variability is homogenized, which could be due to a U-Th zonation, or could be true age heterogeneity. If the sample has true age zonation, homogenizing the material would result in a meaningless average age. Therefore, this is very different to the single-aliquot approach usually employed for these types of samples. Please discuss what differences can exist and how the results will be relevant for a singlealiquot approach.

Our purpose here was to prepare chemically homogeneous powders in order to discuss analytical dispersion using two different analytical methods. This study demonstrates that even on a homogeneous powder, significant dispersion on the U and Th concentrations is encoutered using the same method. We agree that for natural single grain, additional parameter such as U and Th zoning can affect the (U-Th)/He age. We will add more discussion in the next manuscript version about additional sources of age dispersion.

Line 132: *I do not understand this sentence: "The quantitative determination of U-Th abundances can therefore hardly be led on too diluted solutions…"*. *Please re-write to clarify.* 

By "too diluted" we meant U and Th concentrations reaching the detection limit. This sentence is indeed not clear and it will be rewritten.

Line 135: Can you matrix-match your standard solutions to counter these matrix effects? Is this an effective strategy or would removing Fe (like suggested by RC1) produce better results? Did you employ this technique here?

The used standard solutions are in  $HNO_3$  with no iron. This could be interesting to compare these results with concentration resulting from matrix-match solution standard calibration.

Yes, we can purify these elements using Eichrom<sup>©</sup> UTeva B that retains U and Th but not Fe and Al. We have performed experiments to separate these elements for the IF-G sample. We will add in the next version of the manuscript the purification protocol and the results obtained using this protocol. However, our results show that the matrix effects for U and Th content is not responsible for the dispersion of U and Th data. The effect of iron concentration on U – Th determination is actually shown in Figure 5, it can be seen that we reached the necessary dilution.

Line 158: " $45.62\pm3.40$ " and " $116.01\pm12.60$ " contain too many significant figures. Uncertainties shouldn't exceed two significant figures, and the measurement should be rounded accordingly.

Yes, we agree, the two digits is not useful or even meaningful and we will be using 1 digit instead in the modified version.

Line 159: A possible contamination is very concerning. What are the procedural blank levels for these measurements? How many procedural blanks were run? Do the Figure 1: Add 1:1 line to make deviations more apparent.

Four procedural blanks were run and the blank levels for these measurements are 13 picograms of U and 47 picograms of Th.

Figure 2: I'm not sure what the point of breaking the axis is in subfigure (a). There are no values >60% so the axes could just end at 60%.

Ok, the figure will be modified on the next version of the manuscript.

For (b) and (c), adding a line for the minimum uncertainty derived from counting statistics would be helpful. This would show the magnitude of other sources of error, e.g., matrix effects. The analytical trends of uncertainties increasing rapidly below 0.5 ppm are in agreement with my own experience working with similar instruments.

Ok, we will add on these figures the minimum uncertainty derived from counting statistics which are 1.5 % for U and 0.6 % for Th.

Table 2: There is a mismatch between the number of digits for the measurements and that of the uncertainties.

Keep the uncertainties to either one or two significant figures and adjust the rounding of the main values accordingly. Use the same number of significant figures for the mean values and CVs.

Give the full sample names and their abbreviations in the table to make it easier to reference.

Ok, we will add that in Table 2 of the next version.

Also, change "Aluminons" to "Aluminous".

Thank you, we will correct this word.

The absolute measured amounts of U and Th, as well as the measured (or weighed?) Fe-oxide mass should be given for each sample, along with the results of procedural blanks. This would allow a comparison of the measurement and the blank level/detection limit.

Indeed, we have not specified these information which are important. The mass of each analyzed aliquot will be added to Table 2. They all have a mass less than 0.03 g. The blank levels for these measurements are 13 picograms of U and 47 picograms of Th.

Section 3.2: The wording in this section is a bit unclear and should be revised.

Thank you, we will carefully examine the wording of this section to improve it.

Line 189: Change "samples" to "sample".

Ok, we will correct this in the next version.

Line 191: *Change "those" to "this"*. Yes.

Line 192: *Delete "in mind"*. Ok.

Lines 207-209: Did you consider the stability of Th in the solution as a possible cause for dispersion? Th is known to be "sticky", and a high level of acidity needs to be maintained to keep it in solution. Typically, this is done with 5-10% HNO3 and/or by adding a small quantity of HF to the solution. Was the dilution done with water or an acid mixture? How was Th stabilized during dilution? Discuss this here and add a detailed description of the dilution procedure to section 2.3.2.

We do not believe that the dispersion of Th is due to a Th loss from the solution because we ensured that the Th is kept in solution. Indeed, all solutions were diluted with 10 ml of  $0.5 \text{ N HNO}_3$  and 1 drop of HF was added. We will give this information in the next version of the manuscript.

Line 208: Explain what you mean by "over dilution". As the solution is diluted, the U and Th count rates are going to diminish, but matrix effects are going to be reduced. Relative to what do you define the "over" dilution?

The "over dilution" is relative to the blank concentration. If the dilution is too high, although the matrix effect decreases, the concentration of U and Th may be close to the detection limit.

Lines 208-209: The observed natural variability in U and Th concentrations is similar to that of other iron oxides, such as hematite and goethite (see, for example, Hofmann et al., 2020, Chemical Geology). This natural variability, which can be true age inhomogeneity in some samples, highlights the importance of single-aliquot ages that sample small volumes, such as with conventional laser-heating of aliquots in metal packets or laser-ablation.

Yes indeed, but that is not the purpose of our discussion. We are not saying that it is important to crush the sample when dating. We wanted to quantify what causes U and Th concentration dispersion in order to minimize it. Even if all our samples are homogenized by grinding or by synthesis, it is possible to see that the concentration in U and Th is an important part of the error propagated on the (U-Th)/He age.

Lines 257-258: Adjust significant figures as above.

Ok, we will change that in the next version of the manuscript.

Section 4.3: This is a very helpful section!

Lines 288-291: Add references to the relevant literature for these effects.

Ok, we will add references here.

Line 308: The hyphenation of "in-situ" is inconsistent throughout the manuscript.

This is true, we made a choice and used now in-situ.