Emily Cooperdock (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 paper presents U and Th concentration data and uncertainties for select magnetite and Al-spinel samples with a focus on applicability for (U-Th)/He thermochronology. The primary novel contribution of this study is quantifying the reproducibility between wet chemistry dissolution and laser ICPMS results for samples with different concentration levels of U and Th. In the process of completing the study, they test the impact of matrix matched standards for LA-ICPMS analyses. Overall, this study provides a very helpful and useful scientific contribution on our understanding of the analysis and systematics of U and Th in magnetite and spinel. These are very difficult analyses and the techniques are still in the early stages of becoming more widely applicable. Work like this helps push the method forward and has appeal beyond (U-Th)/He dating (for example, economic geology research is also interested in the trace element chemistry of magnetite and spinel and analytical methods).

Overall, I think this manuscript makes an original contribution worthy of publication. Before it is ready to be published, I have several comments, suggestions, and questions for clarification.

Dear Emily Cooperdock, thank you for your interest concerning the manuscript. Your helpful and constructive comments and suggestions will greatly help improving the manuscript. Please find below the answers to the different points you raised.

Specific comments:

1) More sample information should be provided. These tests were run on 2 natural magnetite samples, 1 natural spinel sample, and 2 magnetite synthetic samples. Magnetite grain habits and inclusions suites can vary significantly between samples. Spinel chemistry can vary significantly as well. It is very possible that different magnetite and spinel samples will have different behaviors in dissolution and/or different analytical challenges in terms of matrix effects and U and Th concentrations. The more these samples are characterized in terms of their crystal habit, age, zonation, inclusion suites and any other known geochemistry, the better for future comparison as more studies include more samples. Table 1 is helpful and 2.1.1 and 2.1.2 have some important background information.

Either the main text or the appendix should include more documentation of the sample history and any known geochemical, mineralogy or petrologic characteristics. The study would also benefit from adding photographs of the samples before and after crushing.

It is true that the maximum of information for each sample should be given, especially with respect to possible matrix effects. It is why we have a table (Table 1) which summarizes the necessary information for all samples. In the next version, we will add photographs of the samples (new Fig. 1) at the relevant scale. XRD data for all samples will also be added in the Appendix.

The spinel sample says it is Mg 0.65, *Fe* 0.35 *in Line* 84 – *how was this determined?*

The structural formula was calculated from spinel compositions determined semi-quantitatively by EDS analysis with a Vega3 Tescan SEM at ISTerre (Grenoble, France). The analyzed samples were homogeneous with respect to major elements. This analytical information will be mentioned in the modified manuscript.

XRD determined the synthetic magnetite is 85% magnetite and 15% goethite. Why are the XRD results not included in the appendix?

Effectively, we did not present the XRD results in detail in the previous version to weight down the article, but we agree that the results should be presented and will be in the next version. XRD results of the RB, Al_Spl and IF-G samples in addition to the NMA XRD-pattern will be placed in the Appendix.

We will then mention that XRD data were collected in reflective geometry on Bruker diffractometer (D8 Advance at ISTerre (Grenoble, France).

2) All samples were powdered prior to analysis. Table 1 documents different powdered grain sizes. As far as I know, it is not common to powder aliquots before dissolution during routine (U-Th)/He analysis. A few questions:

Is there any evidence that powder grain size impacts U+Th recovery after wet chemistry dissolution? Or was there any observed relationship between powder grain size and laser ablation conditions (pit size, efficiency, matrix effects)?

Effectively, it is not a common routine to powder the samples before digestion and U-Th analysis. 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.

Is there any evidence that powder grain size impacts U+Th recovery after wet chemistry dissolution? Or was there any observed relationship between powder grain size and laser ablation conditions (pit size, efficiency, matrix effects)?

We do not have any evidence about the powder grain size and the U-Th recovery, for wet chemistry. However, the grain size might influence the laser ablation conditions (inducing nugget effects), therefore we performed our LA-ICP-MS experiments either on finely grained nanoparticules and glasses and we don't have additional information. This is a question for a future study.

The Issua sample is a mixture of magnetite, quartz, and actinolite. Does that mean these analyses included a mixture of these minerals or was the magnetite isolated (I assume not based on Table 1)? If it is a mixture, then what is the justification of using the sample to compare with other magnetite? Would such a mixture ever be used for (U-Th)/He analysis?

We realized that this question was not clearly stated in the original manuscript and will be therefore modified in the next version. The high U and Th dispersion for IF-G sample (20% and 57%, respectively) has been already reported in the literature and could be associated with the mineralogical heterogeneity of this sample which contains not only magnetite but quartz and actinolite as well. This heterogeneity of the sample makes nugget effects possible and is therefore not a good candidate to be used as a reference sample, for U-Th content and (U-Th)/He date analysis.

Is the recommendation of this paper that magnetite and spinel (U-Th)/He should powder samples after degassing and before dissolution? If not, then are the results here translatable to dissolving whole grains? What are the recommendations or warnings to people who may try to do this with whole grains (which is more common for U-Th/He analysis)?

We will effectively add recommendation in the paper. Our advice would be not to crush the samples before U, Th determination, especially when only small amount of material is available, i.e., some milligrams (1 - 3 mg) and when thus a significant part of the material can be lost upon crushing. With spinel the situation is different since grinding is required to achieve digestion. That is the reason why the use of LA-ICP-MS would be a good alternative to avoid grinding and possible sample loss.

3) A significant portion of the manuscript assesses the potential sources for data dispersion, but there is no discussion of the impact of inclusions or intergrown minerals on the results. One of the known issues with magnetite and spinel (and other opaque phases) is that internal inclusions can be present in unknown quantities and can contribute He, or U-Th-Sm, and/or not be fully dissolved, etc. Prior work tries to get around this by using microCT to screen for and avoid inclusions. Here, some of the samples are reported to include mineral phases other than magnetite (Issua and the synthetic magnetite) determined by XRD.

Were the Rocher Blanc magnetite tested for inclusions or intergrown minerals either by microCT or XRD? What about the Al_Spl?

This is effectively a point that we did not raise in the manuscript, considering that it was beyond its scope. To answer some point raised by the two reviewers about the reason of the RB sample contamination, we performed XRD analyses of the powder and detected the presence of calcite, chlorite, titanite in addition to magnetite. It is true that to acquire a large amount of materials (> 1 g), we grind a lot of grains that likely contain mineral inclusions or other minerals at the edge of the grains. In Schwartz et al., (2020) only clean single grains were selected and analyzed. Here, the few percent of titanite and calcite are very likely responsible for U and Th enrichment found in the RB powder. For the Al_Spl, the sample is pure spinel and no mineral inclusions were observed during SEM characterization.

Additional information will be added in the next version, to better emphasize those points.

For this study, how could intergrown phases or inclusions impact the dispersion in the data? How would this vary between the wet chemistry technique and LA-ICPMS?

Indeed, intergrown phases could impact the U and Th dispersion, especially for RB and synthetic nanomagnetite samples that contain titanite-chlorite-calcite and goethite, respectively. However, those samples present quite homogeneous U and Th dispersion for both wet chemistry and laser-ablation. The integration of these samples during U, Th analyses (during both LA-ICP-MS and wet chemistry) are, in our opinion, adequate to be used as standards.

Please include a greater discussion on the possibility for these effects within discussion section. A recent study that showed the impact of inclusion in magnetite on He concentration is Hofmann et al., 2021 "Exposure dating of detrital magnetite using 3He enabled by microCT and calibration of the cosmogenic 3He production rate in magnetite" in GChron.

We will add additional discussion about the effect of inclusion on He budget in magnetite and cite Hofmann et al. (2021).

4) Spinel dissolution can be quite challenging. It would be very helpful to include in the appendix the exact procedure used for others to reference and reproduce. The text mentions that some spinel took multiple rounds of acid attack.

Did the time it took to dissolve spinel trend with data accuracy or reproducibility? It would be very helpful to know if it impacts U and Th recovery or sample loss. If it doesn't impact the data, that would be very comforting to document. If it does impact the data, it will be important to know. It seems that this study can address this question.

We will include additional information about the spinel digestion protocol. We dissolved Al-spinel in 2mL of Savillex with 1.5 mL of aqua regia + 0.5 mL of 29N HF + 2 drops of concentrated HClO₄. Then we put on top of the Savillex a Savillex Ultem® socket, what increased the pressure inside the vial. The Savillex is then put on a hot plate at 130°C. 48 h are enough to completely dissolve the aluminous spinel. HCl, HNO₃ and HF were evaporated at 130°. Finally, HClO₄ was evaporated at 180°C.

5) Many of these analyses are very low concentration and close to blank level. Blanks are not reported. Please add any blank or standard data to the main tables or appendix. Without blanks it is not possible to assess the measurements (were the blank corrected?) and without knowing the blanks reproducibility, it is not possible to propagate the full uncertainty on the measurements, which is central to the study.

Indeed, we did not report the blanks, we will add blank level in the next version as supplementary data. Four blanks were run and the blank levels for these measurements are 13 picograms of U and 47 picograms of Th.

Line Comments (some may be repetitive with the comments above):

45: "is very little soluble in minerals" should be corrected to "He is not very soluble in minerals" or "has low solubility in minerals" We agree we will correct this sentence in the next version of the manuscript.

53: Sentence starting "In addition, well characterized..." is clunky and should be rewritten.

We agree and we will rewrite this sentence.

75-85 (2.1.1.): I'm left wanting more information on the samples. Please include more details. Also, how was the spinel composition determined? Microprobe?

XRD data and photographs of each sample will be given in the next version of the manuscript. We will explain that the spinel composition was determined by scanning electron microprobe (EDS).

93: The natural samples and synthetic samples have different grains sizes after powdering. Does this difference in grain size make a difference in the analyses?

We have no evidence of any grain-size effect on U and Th data obtained by wet chemistry (digestion). Whereas RB sample grains are micrometer-sized and NMA grains are nanometer-sized, they give similar U and Th reproducibility, 6.5 and 2.6%, respectively, for RB, and 7.4 and 5.4%, respectively, for NMA. Therefore, small grain sizes do not improve reproducibility

100: The samples were ground up before dissolution. Is this a requirement for dissolution?

We ground the samples in order to get ca. 2 grams of homogeneous product to perform both LA-ICP-MS and wet chemistry analyses on the same samples.

What mass was dissolved per aliquot?

The dissolved mass is always less than 0.03 g. The exact mass of each aliquot will be given in Table 2 in the next version.

Is powdering samples reasonable for typical (UTh)/ He analysis or would it need to be modified?

No, as we will explain in the next version of the article, it is better to avoid grinding the sample before dating because during grinding part of the material can be lost and thus (U-Th)/He age determination may be altered.

125-129: Was there a trend in dissolution steps vs U+Th recovery for spinel? Does it affect the accuracy of the measurement? What are microbombs?

I am not sure I understand this question since we did not follow a step dissolution. Spinel was dissolved with the same method used for magnetite. The micro-bombs that we used are Savillex with a closing lid (Ultem® sockets).

134: Spinel can contain variable amounts of Fe, Al, Mg, and Cr beyond what is listed here. The chemistry likely makes a difference in the way it dissolves and potentially could relate

This is true, our dissolution protocol only applies to aluminous Mg-spinel. We are working on the dissolution of Cr-spinel which is indeed abundant in ultramafic rocks.

134: "The direct analyze" should be "The direct analysis"

Yes, we will correct this sentence.

135: Can these elements be removed via column chemistry? Do your results suggest that is an important step to avoid matrix effects?

Yes, we can purify these elements using Eichrom[©] 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.

159-163: This is a very interesting observation (that the powdered samples are 100x higher in U+Th than measured by Schwartz et al., 2020). You say it could be contaminated with U+Th. Is that during preparation? Or is it possible that powdering grains included a lot of inclusions that Schwartz et al 2020 avoided by CT scanning their grains prior to analysis?

Yes, we expect some "contamination" from ca. 4 wt.% of calcite and 2% of titanite (XRD data). Actually, contrary to Schwartz et al. (2020) we ground a large amount of sample (ca. 2 g) and mineral inclusion/coating may have been present in the sample. Furthermore, the grains were not checked with CT scan for purity.

How much sample was powdered to produce the homogenous, enriched U+Th in this study?

2 g of each sample were powdered.

Was the same powder split and used to make the pellet for LA-ICPMS?

Yes, that is why we ground large quantities of material (2 g) and synthesized large quantities of nanomagnetite (12 g) in order to be able to analyze them by wet chemistry and laser ablation and then compare the results. We will add more details in the next version of the manuscript to be clearer.

169: "*The dispersion is more important for Th*" – *do you mean more important or larger*?

Yes, we meant "larger" and we will change it in the next version.

171: *Have you considered that the larger Th dispersion is due to Th falling out of solution? This is often a problem for wet chemistry analyses.*

No, because we tried to minimize the loss of Th in solution by the systematic addition of HF in our beakers which keeps Th in the solution.

Alternatively, Th wash out times on ICPMS can take significantly longer than U and other elements. Sometimes Th takes a long time to reach the detector compared to U and other elements. Could either of these issues be a possibility for the Th uncertainty?

No, because the required washing time has been optimized on Th-bearing samples. Washing between two samples was performed with a mixture of $HNO_3 + HF$ during almost 4 min before analysis. This "long" washing sequence allows to remove all the remaining Th in the ICP-MS between each analysis.

Figure 2: Th dispersion appears to be concentration dependent, but also sample dependent. Your IF-G sample appears to have the highest dispersion and lowest concentrations which makes sense with analytical limits on uncertainties. But it is also a sample with three intergrown minerals. Could some of the dispersion be due to heterogeneous mixtures or nugget effects?

Indeed, the heterogeneity of the IF-G sample could create a nugget effect on the U and Th results, and the dispersion of the U and Th concentrations is surely partly due to this. We will add further explanation in the article to discuss this option.

How much sample was homogenized and how large are the aliquots that were analyzed?

We homogenized 2 g of RB magnetite grains and 2 g of Al_Spl (single crystal). The weight of the aliquots is always less than 0.03 g and we will specify each mass in Table 2 in the next version of the manuscript.

Line 206: What does "contrasted values" mean?

We wanted to mean that the values are scattered. We will rewrite this sentence in the next version.

Figure 4: I note that the sample weights that I asked about in my previous comments are plotted here. Can sample weights be added to a results table so that the reader can reference it more easily throughout the text?

We agree. We will add the weight of the aliquots in Table 2 of the next version of the manuscript.

240: Interesting that the glass standards made the LA-ICPMS RB samples 30% higher than the wet chemistry method, which are already 100x higher than Schwartz et al., 2020. Can you expand more on why this matrix effect causes higher concentrations (rather than lower or dispersed)?

Yes. As shown in Figure 3 of the manuscript, the slope of the calibration line obtained with glass standards is greater than the slope of the calibration line obtained by adding NMA as a standard. A greater slope will result in apparently higher U and Th concentrations.

We do not not have a clear physical explanation but clearly silicates and oxides react differently to laser ablation and behave differently in the mass spectrometer (see Wilson et al., 2002 published on the *The Royal Society of Chemistry* or Steenstra et al., 2019 published on *the Journal of Analytical Atomic Spectrometry*).

261: There are other studies that have performed LA-ICPMS on spinel in the literature that should be cited here and can be used to discuss how others have matrix matched their standards or any implications your study has on these prior studies. For example, Colas et al., 2014 "Fingerprints of metamorphism in chromite: New insights from minor and trace elements" in Chemical Geology is one but there are others as well.

Thank you, we were not aware of this article which is very relevant to the present study. Actually, the source article is Locmelis et al. (2011) which presents the natural spinel standard used by Colas et al. (2014). Locmelis et al. (2011) and Colas et al. (2014) used the sample standard as an "unknown" sample to verify the accuracy and the precision of LA-ICP-MS analysis. They do not use as an external standard in order to avoid matrix effects.

290-300: This section of the discussion offers no reference to the impact of inclusions on dispersion in magnetite and spinel. This should be added.

We will discuss the impact of inclusions on dispersion in the next version. Thanks to grinding, the RB powder is homogeneous in U-Th concentration despite the presence of mineral inclusions. The results

of U and Th analyses on RB are very little dispersed compared to other samples and IF-G in particular. As already discussed here, IF-G sample may exhibit nugget effect.

297: The laser ablation parameters should be reported in a table in the text or appendix. How many spots per sample? Were spots averaged? Were some samples/spot sizes under the detection limits? What was the variation in U and/or Th recovery with spot size?

All these information will be reported in the next version. We made 10 spots of 160 μ m diameter per sample. The location of the spots was chosen so that all the sample surface was covered in order to verify the homogeneity of the pellets. No sample was below the detection limit and all are presented in Table 3.

310: Do you think the dispersion (20%) is primarily an analytical limitation or a geologic limitation?

It is only an analytical limitation in our study because our samples are homogeneous and so we do not consider the geologic part.

356-362: This discussion on the location of U in the synthetic magnetite is super interesting. A big question is whether U can be incorporated into the crystal structure or is adsorbed onto the surfaces and the magnetite grows around it. It can have important impact on dissolution and He production. I wonder if this discussion can be moved into the main text?

We prefer that this part remains in the Appendix in order not to weigh the article down.