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Comment on egusphere-2022-520

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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, https://doi.org/10.5194/egusphere-2022-520-RC1, 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.

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.
- The spinel sample says it is Mg 0.65, Fe 0.35 in Line 84 – how was this determined?
- XRD determined the synthetic magnetite is 85% magnetite and 15% goethite. Why are the XRD results not included in the appendix?

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)?
- 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?
- 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)?

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?
- 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? 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.

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.

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.

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"

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

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?

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?

100: The samples were ground up before dissolution. Is this a requirement for dissolution? What mass was dissolved per aliquot? Is powdering samples reasonable for typical (U-Th)/He analysis or would it need to be modified?

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?

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 to U+Th concentrations. It's beyond the scope of this study, but worth noting here that there is a solid solution to consider.

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

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

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? How much sample was powdered to produce the homogenous, enriched U+Th in this study? Was the same powder split and used to make the pellet for LA-ICPMS?

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

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. 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?

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

Line 206: What does "contrasted values" mean?

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?

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)?

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.

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.

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?

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

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?