EGUsphere, referee comment RC2
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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-RC2, 2022

Review of Corre et al., submitted to Geochronology

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.

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”.

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

Line 42: Change “fault” to “faulting”.

Line 45: Change “radiogenic” to “radioactive”.

Line 46: Change “neighbor” to “neighboring”.

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 ^{4}He to a level above that of the measurement uncertainty. For most samples, the contribution of Sm to the measured amount of ^{4}He 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.

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

Line 93: Was the goethite removed before analyzing the magnetite? Were U and Th partitioned between the magnetite and goethite? Please discuss this possibility and mention any data you might have.

Line 100: Why were the samples ground into a powder? 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 single-aliquot approach.

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.

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?

Line 158: “45.62±3.40” and “116.01±12.60” contain too many significant figures. Uncertainties shouldn’t exceed two significant figures, and the measurement should be rounded accordingly.

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.

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%. 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.

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. Also, change "Aluminons" to "Aluminous". 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.

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

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

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

Line 192: Delete "in mind".

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% HNO_3 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.

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?

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.

Lines 257-258: Adjust significant figures as above.

Section 4.3: This is a very helpful section!

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

Line 294: Do you mean (>10%)?

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