

Geochronology Discuss., author comment AC2  
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## Reply on RC2

Cécile Gautheron et al.

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Author comment on "Technical note: Analytical protocols and performance for apatite and zircon (U-Th)/He analysis on quadrupole and magnetic sector mass spectrometer systems between 2007 and 2020" by Cécile Gautheron et al., Geochronology Discuss., <https://doi.org/10.5194/gchron-2021-1-AC2>, 2021

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Dear reviewer RC2,

Thanks for your positive and constructive review, that highlight some unclear sections. We made the required corrections, and we are given a lot of details, especially on  $^4\text{He}$  sensitivity determination of the quadrupole and magnetic sector mass spectrometers. Some suggestions were similar to the one raised by reviewer RC1, and all suggestions were taken into consideration.

In the following, detailed responses are given in bold

All the best

Cécile Gautheron, on behalf of the co-authors

### **General comments:**

This paper presents a very detailed, start-to-finish (i.e. whole rock to publishable dataset) methodology for the determination of (U-Th)/He ages from single grain apatite and zircon crystals. While much of this information is available to the community through the plethora of papers utilizing these methods over the last two plus decades, this work provides a single, succinct source for researchers to consult and cite. Additionally, this paper provides many additional details not commonly published, which, among other uses, is a significant resource for those interested in developing the ability to make (U-Th)/He age determinations in their own laboratories. No major revisions or changes to the paper structure are required. However, I believe minor additional details or clarifications would be beneficial, which are outlined in the line-by-line comments below. Most importantly, clarification to how He tank standards are calibrated for use on either the quadrupole or magnetic sector instruments is required.

### **Line-by-line comments:**

Line 13: Would "we detail the complete protocols in use for more than a decade" be more clear?

**Ok, yes, we changed this section**

Line 15 and line 20: Sensitivity instead of "sensibility"

**Done**

Line 33: "homemade" is used a number of times in this manuscript but "housemade" or "built-in-house" may better describe the laboratory quality of this equipment.

**Ok thanks, we replace all homemade by built-in-house**

Line 33 to 34: "noble gas extraction-purification lines, one coupled to a quadrupole mass spectrometer and the other to a magnetic sector mass spectrometer" may clarify to the reader these are completely separate setups.

**Done**

Line 41: All methods in this manuscript described by the authors are suitable for the described purposes but it may be helpful to show that these methods are not the sole way to accomplish (U-Th)/He age determinations. Here, offering LST as a less toxic alternative to the already mentioned heavy liquids may be useful.

**Yes, good point, we added a new sentence saying the LST is a less toxic alternative**

Line 61 to 62: The possibility of Nb packets influencing the measured [U] and [Th] is certainly of concern. If this issue is going to be mentioned in section 2.1 then it may be worthwhile to tell the reader this point will be discussed at length later in the manuscript and the current texts leaves the reader feeling like this issue remains completely unresolved.

**We add a sentence saying "The Nb impact on the U and Th content determination will be discussed in detail in section 3.3." (section numbers changed)**

Line 66: Since both extraction lines described in the manuscript are being presented for the purposes of measuring He, a name such as "Quad line" instead of "He line" may help the reader more easily identify the two.

**Good point, it is just an old habit. We are now using the 'Quad line' name instead of 'He line'**

Line 74: Figure 1 has many details not discussed in this paper. May be worth a short comment about features such as the He diffusion cell or the exclusion of those portions from the schematic.

**Yes, we agree that the He diffusion cell part is not used in this study, however, we keep it, as it is part of the line volume and design. We add a sentence in Figure 1 legend to state so.**

Line 84 to 86: Since only the planchet and line before first valve would see atmosphere, is the described heating targeted at just the planchet or the entire extraction and cleanup line? How is the heat applied?

**We agree that this part was unclear, and we rephrase it. We are heating the whole line using a heating tape at low temperature (<50°C). We changed the paragraph to better explain the protocol we are using.**

Line 93: It is worth noting here that a shorter but hotter zircon degassing conditions are

also possible.

**Done, we added a sentence associated Table 1, where we also gave information about apatite. "apatite and zircon can be heated at different temperatures and with different time lengths, especially zircon that should be heated at higher temperature. Equations established by Fechtig and Kalbitzer (1966) can be used to calculate the minimal time, for a given temperature, that should be used to ensure complete He degassing, knowing the He diffusion coefficient. It is, however, important to not heat apatite crystals at too high temperature to reduce any issue with U or Th volatilization."**

Line 94 to 95: What threshold (percent?) is used to identify an acceptable return to background level signal?

**We added the information that it is 2%**

Line 103 to 106: The method to measure temperature is calibrated to 1150° C but the zircon setpoint is stated to be >1250° C. How is the temperature monitored during degassing of zircon?

**Yes, good point, it was a mixing with the VG line, where we can record higher temperature with the diode laser system. We correct the sentence and add information about the monitoring. We added the following details:**

**The protocol has been built for the purpose of degassing apatite crystals or fragments that are packed in a Pt tube, where the chosen heating time and temperature schedule should permit to retrieve all the He from apatite during the first degassing step, as predicted using the mean diffusion coefficient of Farley (2000) for Durango apatite. If the unknown apatite is pure and presents a diffusion coefficient similar to the Durango apatite, the He content of the second step should be similar to background. This protocol thus allows to detect any He retentive mineral inclusion (e.g., titanite, zircon) that was not seen on picking and contributes to the He budget (Farley, 2002). It can also be used to monitor the retentiveness of apatite crystal associated with the impact of radiation damage. For zircon, as mineral inclusions are not an issue for (U-Th)/He age interpretation, we simply heat the Nb capsule at a temperature close to image color saturation (~1200°C; Fig. 2) and ensure to avoid any overheating problem such as capsule melting. Although Pt and Nb have different emissivity values, the temperature calibration is not adapted to Nb. Indeed, the visible color for a given temperature is not the same for Nb and Pt capsules. Nevertheless, the zircon crystals can be heated until total He degassing, and neither the poor determination of the heating temperature nor the different emissivity values are an issue.**

Line 126: At what temperature are each SAES getter operated at?

**Yes, good point, we added the information that we are using the SAES at room temperature**

Line 136: C+++ may be a concern for low <sup>4</sup>He abundance measurements. Is mass 6 (C++) monitored for this concern?

**No, we never tried on the quad line, but thanks we will. For low apatite crystal content, we are using the VG line where the sensitivity is slightly better.**

Line 137: Longer gettering time could be offered as a suitable alternative to reduce the H<sub>2</sub>

influence on  $^4\text{He}$  peak if one does not wish to add a getter after mass spec inlet valve.

**We added a comment to offer this option to readers.**

Line 146: It is unclear to me if " $^3\text{He}_c$  is the  $^3\text{He}$  content value adapted for each calibration" means each  $^3\text{He}$  spike tank is calibrated at the start of that tank's use or if this is a determination made during each batch of analyses. Is  $^3\text{He}_c$  calibrated manometrically (or against another known tank) or is calibration solely done with Durango standards?

**We are calibrating the  $^3\text{He}$  tank using only the Durango standard, and only empirically. That is a very unexpensive solution, as calibration with a known tank or using a manometric experiment is more costly. We added a sentence to describe it.**

Line 164 to 165: Again, it is unclear if the tank shot is initially calibrated manometrically then tweaked from Durango standards that are specific to the analysis batch.

**Good point. We clarified the text by adding information. In fact, we are not using the  $^4\text{He}$  tank to calibrate the sensitivity, but we are using it to follow the source stability and signal reproducibility.**

Line 183 to 184: It is unclear to me here if the authors are describing a test to verify this outlined cleaning procedure is adequate or if they are describing a procedural blank carried out with each batch of analyses.

**Sorry it was unclear. We rephrase the sentence.**

Line 225: The  $^{235}\text{U}/^{238}\text{U}$  value of 0.00725 is equivalent to  $^{238}\text{U}/^{235}\text{U}=137.93$  (different from the more commonly used 137.88 referenced on line 288). For consistency, I suggest only referencing  $^{238}\text{U}/^{235}\text{U}$  with a value of 137.88?

**Yes there is indeed a small difference with 1/137.88 being 0.00725268 not 0.00725. Ok, we correct it, and we introduce both notations, but we keep the 235/238 ratio because we are always using spike/natural**

Line 289 to 290: Another word besides "important" may better describe the linearity effect below 150 Ma. How is data processed for samples with ages >150 Ma?

**We replaced the word important by 5 to ~600 time higher compared to 150 Ma**

Line 310: Do the author's have an explanation regarding the two  $\text{H}_2$  spikes observed (nearly two orders of magnitude increase in signal size)? Considering the  $\text{H}_2$  tail can influence the  $^4\text{He}$  signal, a comment regarding whether spikes such as these should be used to alert the user to be suspect of the  $^4\text{He}$  measurement would be useful.

**Yes, we detect a very high  $\text{H}_2$  signal that was due to a purification problem related to one nonfunctioning valve. We added the following sentence: "In addition, we are following the  $\text{H}_2$ ,  $\text{CO}_2$  and Ar signals to guard against any leak and gas purification problem. For example, on figure 3B, the  $\text{H}_2$  signal was higher than usual (pipette number of 200 to 250) and helped to alert about a technical problem related to purification. It will then help to take the AHe ages with caution for low  $^4\text{He}$  samples, considering the  $\text{H}_2$  tail can influence the  $^4\text{He}$  signal."**

Line 322: Deleting "to mostly" may make this sentence read more clearly.

**Done**

Line 315 to 326: It is difficult for me to follow the details of the quad line standardization and I think this section could be improved upon with some clarification. Specifically, when exactly is  $^3\text{He}_c$  and D determined? Is it done for every batch of analyses? The comment about 1 to 2 months is confusing. Is that just the timeframe that variation is typically observed over?

**Sorry, it was unclear. We are analyzing the U, Th, Sm and Ca content every 1 to 2 months of analysis, and then are calculating the (U-Th)/He ages of Durango standards. Hence, we can calibrating the D and  $3\text{He}_c$  value after every batch. However, most of the time those D and  $3\text{He}_c$  values are not changing. But they can differ significantly after power breakdown, that happen too much at Paris Saclay University...**

Figure 4 shows some Durango ages (panel C and D) that considerably differ from the acceptable (U-Th)/He age. How is data like this handled? Is some sort of outlier detection utilized? Are  $^4\text{He}$  measurements of unknowns run in batch sequence proximal to these outliers being processed (or rejected) using these outlier Durango ages, such as seen on panel C and D? If so, how?

**We changed the 3.1. paragraph in order to add more details about how we are performing the calibration for the Quad line, and how outliers are used to test for any problems. We add the following sentence for the specific problem of outliers**

**Secondly, we are also checking for any analytical issues the apatite (U-Th)/He ages, including Durango apatite, during the analysis batch. As observed on Fig. 4C-D, three Durango ages are lower or higher than the expected age of  $31.02 \pm 1.01$  Ma from McDowell et al. (2005). Those outliers can indicate either that the Pt tube was too closed, preventing the acid from penetrating into the closed tube, or an issue during acid digestion, or an analytical issue during ICP-MS analysis, or a too high heating temperature that has vaporized U and Th, or any issue during He quadrupole analysis. Because, in quadrupole gas analysis, we are recording the tube temperature during heating of sample and backgrounds, the issue should be related to a digestion problem or the ICP-MS analysis. For the cases presented on Fig. 4C-D, the lower ages were associated with Th/U ratios that are significantly different from other aliquots, tracing the incomplete recovery of the U, Th and Sm content associated with non-total digestion or clogging of the solution during ICP-MS analysis. We thus check, for unknown samples, any digestion or ICP-MS issue.**

Line 324: Sensitivity instead of sensibility?

**Done**

Line 340: Does "To better calibrate the  $^4\text{He}$  cylinder" imply the cylinder is calibrated in another fashion (e.g. manometrically or against another known tank)?

**Yes, good point, we remove better, as the  $4\text{He}$  tank is calibrated against Durango apatite.**

Line 343 to 359: As with the quad line section above, it is unclear exactly when sensitivity is determined for the VG instrument. The text reads as if the instrument sensitivity has only been determined twice. Is there a "D" type factor used to tweak the instrument sensitivity for each run? Currently the text reads to me as if sensitivity is not determined for each batch of analyses, which I would consider necessary for the determination of

absolute quantities of ions such as is required for (U-Th)/He age determinations.

**We rewrite this section to be clearer. We also add a sentence explaining that we are using the 4He tank only for checking of signal reproducibility.**

Line 402 to 405: Using the phrase "needs to be considered" in this sentence could be misinterpreted as a correction is not currently being made (although my interpretation of the text is that a correction is made using the measured parent isotope ratios of the different blank).

**Yes sorry, it was unclear, and we remove 'need to be considered' and we are now using "is considered"**

Line 440: I assume the Ma is not needed here.

**Yes effectively, we removed it**

Line 545: say "in use for more than ten years" or "developed over the last ten years" instead of "developed for over more than ten years"?

**Changed and we are using "developed over the last ten years"**