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Interactive comment on "U–Pb geochronology of epidote by LA–ICP–MS as a tool for dating hydrothermal-vein formation" *by* Veronica Peverelli et al.

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Dear Editor,

Please find below the response on behalf of all authors to the comments posted by James Darling (Referee #2) on our manuscript "U–Pb geochronology of epidote by LA–ICP–MS as a tool for dating hydrothermal-vein formation" (MS id: gchron-2020-27).

The response is laid out as follows: we start by grouping comments that were raised several times into "General issues". We then provide a "Response" to each individual

"Referee comment", indicating in brackets the manuscript lines or sections as reported by the referees.

The following color code applies: GREEN = General issue; BLUE = Referee comment; BLACK = Response.

We hope that you will find this response satisfactory.

Yours sincerely, Veronica Peverelli, on behalf of all authors

General issues:

1. Documentation of correction for downhole fractionation The referee points out that in Fig. 4b,c and 5 some of the lines representing time-resolved (total) 206Pb/238U ratios are not flat despite having been corrected for downhole fractionation. This is indeed true, and after re-evaluation of the data we have established that this is due to zoning in initial Pb contents in most cases. This was verified by applying a 208Pb correction with values calculated from the Tera-Wasserburg diagram. After this, most of the sloped lines become flat, demonstrating that the correction for downhole fractionation worked properly. However, some analyses still displayed some sloping in the time-resolved (radiogenic) 206Pb/238U ratios even after the application of the 208Pb correction. We therefore decided to exclude these suspicious analyses from the dataset for age calculation, and obtained ages and initial 207Pb/206Pb ratios that are within uncertainty of those presented in the first version of the manuscript. The effects of variable initial Pb contents on the accuracy of analyses as well as the need to carefully assess 208Pb-corrected time-resolved 206Pb/238U ratios after correction for downhole fractionation will be discussed in section 4.2 of the revised version. Updated figures, ages and isotopic ratios will be included in the revised manuscript.

2. Sample Grimsel-1 data Following "General issue #2", some analyses were excluded from the dataset for age calculation. We appreciate the suggestion of the referee to combine the 50- and 30-micron datasets, and this possibility will be addressed in

the revised manuscript. We also considered the proposed geological interpretation of the obtained ages as reflecting partial reset of this epidote sample during subsequent deformation. We recognize that sample Grimsel-1 is texturally and geochronologically complex. A work on epidote microstructures and their relationships with trace element and isotopic data is currently being carried out, and it would be outside the scope of this methodological contribution. However, we agree with the referee that partial resetting cannot be ruled out, and we will hence discuss the referee's hypothesis in the revised text.

3. Comments on the use of the phrase "monoclinic epidote" Our epidote samples are compositionally within the epidote-clinozoisite solid solution and we agree that the phrase "monoclinic epidote" is inaccurate. A clearer definition of the use of the term "epidote" will be given in the revised text and the manuscript will be edited accordingly. The fractions of epidote (XEpi) and clinosoizite (XCzo) components will be added in section 4.1.

Referee comments by James Darling:

1. "The text needs to make a clearer distinction between epidote supergroup minerals and epidote here. Oberli et al., (2004) measured grains varying from low to high REE+Th contents (i.e. "allanite")" (lines 44-51) See "General issue #3". Oberli et al. (2004) also report one analysis on epidote (i.e. epidote-clinozoisite solid solution; their section 5.3 and their figure 5). It will be made clear in the revised text that we refer to this one analysis.

2. "epidote supergroup minerals can have wt. % levels of Th (i.e. allanite)" (lines 45-46) See "General issue #3".

3. "several papers have presented methods for monoclinic epidote group minerals (typically those with a high allanite component). Given that the supergroup contains sold-solution series, the distinction between epidote and epidote supergroup minerals needs to be made much clearer here - especially as magmatic allanite used as primary

reference material - doesn't really seem right to say that no one has done this before unless you more specifically mean end-member epidote. Could also mention here that the protocols in this study are very similar to those applied to apatite. See also Conclusion Line 564 and elsewhere in the text, where use of 'monoclinic epidote' is a bit vague in this regard (as this could include allanite)." (lines 58-60) See "General issue #3". The similarity with the protocols applied to apatite will be acknowledged in the revised text.

4. "It has also been shown that DF can be minimized to the point of not requiring matrix-matched standardization (https://doi.org/10.1016/j.chemgeo.2011.11.012). It would be good to acknowledge this here, because it provides an alternative approach for U-Th-Pb isotope analysis of allanite (epidote supergroup minerals)." (lines 99-103) The possibility of non-matrix-matched standardization will be mentioned in the revised text.

5. "again, here the text gets a bit muddled between epidote supergroup minerals and epidote group minerals (for the latter it is claimed that no previous geochron work has been undertaken in Line 58). Epidote supergroup minerals with a high allanite component are also monoclinic - so use of 'monoclinic epidote' here is not clear in meaning." (lines 107-110) See "General issue #3".

6. "it is incorrect to say that 204Pb corrections are not possible from LA-ICP-MS data. See https://doi.org/10.1016/j.chemgeo.2011.11.012 and especially Cenki-Tok et al., (2014: https://doi.org/10.1111/ter.12066)." (lines 115-118) Agreed. We will rephrase the text to clarify that a 204Pb correction is complex and we thus prefer to use the Tera-Wasserburg approach, which uses ratios that are not corrected for initial Pb. We will also acknowledge the possibility of correcting for initial Pb by measuring 204Pb in coexisting mineral as done by Cenki-Tok et al. (2014).

7. "I think that a statement should be added here making it clear that it has been shown in many papers that Stacey & Kramers model values are often not appropriate for correcting allanite, titanite, rutile etc U-Pb ratios, and hence extreme caution is

required here." (lines 117-121) We agree. In fact, we do not correct Tara allanite by using Stacey & Kramers (1975) model values – as erroneously stated in the text. Instead, we determined the initial 207Pb/206Pb ratio from a Tera-Wasserburg diagram that we created based on the TIMS data reported by Smye et al. (2014). This was the value used to apply the 207Pb correction to Tara allanite. This value is already reported in Table 2, and the text will be edited accordingly.

8. "detail of the DF corrections applied is missing here. How was DF modelled and corrected in Iolite?" (lines 215-220) We selected an exponential function to correct for downhole fractionation in Iolite. Iolite fits this functions to model the downhole fractionation on primary reference materials, then applies this function to all unknown analyses to correct them for downhole fractionation. This will be specified in the revised text.

9. "Do the final uncertainties provided for unknowns include propagated uncertainties from the 207Pb-correction of Tara (including uncertainty in initial Pb composition and correction)? Please specify. If not, these sources of uncertainty should be fully propagated through to the results." (lines 224-226) The VisualAge_UcomPbine package used on Iolite for data reduction is described by Chew et al. (2014). Although the authors do not specify whether or not the uncertainty coming from initial Pb correction is propagated onto the unknowns, an overall uncertainty coming from the reproducibility of the primary reference material is propagated by Iolite.

10. Please summarize here or in Table 3 the effect on precision of anchoring the 207Pb/206Pbc. (lines 229-234). This will be done in the revised manuscript.

11. "No mineral chemistry is presented for the studied epidotes. Are there independent constraints on the composition of these grains? Given solid solution with clinozoistite, it would be useful to know if there is any relationship between major element chemistry and U/Th/Pb contents, as well as possible links with matrix effects." (section 4.1) A study on mineral chemistry is part of ongoing work. A consideration of matrix effects related to mineral chemistry, although captivating, goes beyond the scope of this con-

tribution. From the present data it can nonetheless be stated that, since MSWD is low in all our Tera-Wasserburg diagrams, matrix effects – if any – have no effect at the current analytical precision.

12. "As above, how was DF corrected in iolite? I've not seen details documented anywhere as yet (function used?)." (lines 324-345) See "Comment #8".

13. "The discussion of DF in unknowns is very cursory and some additional analysis seems to be warranted by the data. The text states that all of the unknowns have 'parallel flat lines' on Figure 4, but this is not correct. Focusing on Figure 4C, there are analyses that have decreasing ratios through time, and others that have increasing ratios. This indicates that the assumption of exact matrix matching between Tara and all of the unknowns is not perfect. To me, it seems likely that the DF correction is working within the large uncertainties of individual measurements, but a more detailed analysis of this issue is warranted. What are the differences between analyses with +ve and -ve slopes here (compositional?) and what is the likely effect on accuracy and uncertainties? These issues need to be acknowledged in the main text and at a minimum state that the DF correction seems to be working within large uncertainties of individual epidote measurements. - it is possible that this variability is caused by zonation in concentration, rather than a matrix effect. The presentation of data on Figure 4 is not very clear, which limits the ability to really resolve these issues. You could present these as % change in the ratio through time, and either select a subset of analyses that have independent measures of heterogeneity or average data from each X second time interval since shutter opening." (section 4.2 and figure 4) "as per previous comment, some of the ablations shown are certainly not "flat" when it comes to DF-corrected 206Pb/238U. This should be acknowledged in the text and a more detailed analysis provided. At lease one measurement on Fig. 5a has huge variation in the ratio - linked to variable U +/- Pb contents, or weird ablation behaviour?" (figure 5) See "General issue #1".

14. "There is a bit of an issue with the Grimsel-1 data here. For the 30 micron data,

the text states that 4 data points were rejected on the grounds that they 'cause higher MSWDs'. However, it is correctly noted in the intro to T-W plots that scatter can reflect non-cogenetic origins (and hence have important geological meaning). To test this, I replotted the 30 micron data using IsoplotR; using all 25 data points I get a resulting T-W intercept age of 17.25 +/- 11.15 Ma (95 % conf.; MSWD = 1.2). I do not see any obvious reason to exclude any of this data (especially as IsoplotR includes scatter in the 95% conf. uncertainties). One issue, the 7/6 intercept on my plot is 0.7863 +/- 0.0051, which is JUST outside of uncertainty of the initial on Figure 6b. Could this reflect either (a) underestimation of uncertainty in the 50 micron data (note MSWD <1) or sampling of external Pb using larger spot sizes (i.e. modern lab Pb)? Please replot the 30 micron data to check all of this, and I don't think that grounds to exclude points are strong. Following on from that, why not combine the 50 and 30 micron data for Grimsel-1 into a combined T-W? I did this, and get a result of 15.69 +/- 5.94 Ma (95 % conf.; MSWD = 2.6), with initial 7/6 of 0.7922 +/- 0.0033. The distinction could be important, as the ages for ductile deformation in the area from Rolland et al., (2009) are ∼21 Ma (Stage 1) and ∼14-12 Ma (stage 2), and these authors speculate that brittle structures formed at ∼15.5 Ma. Could the higher MSWD of this regression be reflecting some epidote growth/resetting throughout this complex deformation history?" (Data for Grimsel 1, lines 388-398) See "General issue #2".

15. "change 'used to normalize the measured isotopic ratios to real values after correcting them for DF' to used to correct measured isotopic rations for DF." (lines 466-467) This will be done in the revised text.

16. "as per previous comment, the corrected ratios shown are not all "flat", so this needs to be changed and a more complete analysis of DF corrected ratios presented." (lines 467-470) See "General issue #1".

17. "I found this section quite repetitive, and some of the key points (spread & sample volume) have already been made in the previous section. It would be useful to restructure and refine Sections 5.2 and 5.3 to produce a more focused and less repet-

itive discussion." (section 5.3) We will rephrase and shorten section 5.3 in the revised text. However, sections 5.2 and 5.3 address two separate issues: one dealing with the appropriateness of the correction for downhole fractionation with different spot sizes, and the other dealing with the effects of analytical uncertainty on the quality of the regression. We therefore prefer to keep them separate.

18. "The Cenki-Tok et al., (2014) paper provides an excellent example of the need to independently determine initial Pb compositions to correct allanite analyses. I reccomend mentioning that study at this point of the discussion." (section 5.4) See "Comment #7".

19. "as per previous comment, the existing geochron in the Grimsel area is a bit more complex than shown in the discussion here. Rolland et al., (2009) document two distinct ductile deformation phases at ∼21 Ma and 14-12 Ma - is there particular evidence to suggest that the epidote bearing veins are only recording the earlier episode? Perhaps epidotes in these folded veins are being partially reset during the younger ductile event?" (lines 523-529) "The discussion of the Grimsel vein results may need tweaking given the slightly younger age determined from the combined 50 and 30 micron spot data. Unless there is a clear reason not to combine these datasets, the slightly younger age and higher MSWD could have bery interesting implications for the significance of epidote ages from these samples...." (lines 545-555) See "General issue #2".

20. "should read 238U (rather than 283U)" (abstract, line 8) It will be corrected in the revised text.

21. "Would be useful for the text here to be a bit more specific on what is meant by 'appreciable', and also which aspects of the initial Pb are variable (presumably this primarily refers to concentration?)" (abstract, lines 14-15) This does refer to the contents of initial Pb relative to total Pb. The revised text will be rephrased and fractions of 206Pb added to the data.

22. "It is possible for epidotes in a sample to be cogenetic (formed during

the same event) and still record variable initial Pb isotope compositions, e.g. https://doi.org/10.1007/s00410-003-0494-6" (abstract, lines 20-21) This aspect will be acknowledged in the introduction in the revised manuscript.

23. "Need to split this into two sentences." (lines 80-84) "minerals" (line 93) These corrections will be made in the revised text.

24. "is a lenghty description here of the Tera-Wasserburg diagram approach. Given that this is widely used in the accessory mineral geochron community, perhaps this description is not all needed and instead the text could focus on issues relating to epidote geochron more specifically (e.g. U contents, initial Pb variability). There also is some repetition here (fraction of initial Pb; upper 207Pb/206Pb)." (lines 83-96) The manuscript is intended for non-geochronologists as well. Therefore, some introductory information about the Tera-Wasserburg diagram should be given. We preferred to address the effects of U contents and initial Pb variability in sections 5.3 and 5.4 because the discussion can be directly related to the presented data. We will revise the text to avoid any unnecessary repetitions.

25. "there are two (b)s and no (c) listed" (figure 6, caption) This will be corrected in the revised manuscript.

26. "what did the MatLab script do?" (figure 7, caption) We applied a simple fit to the data using a first-order polynomial. The uncertainty envelope is at 1σ level. This will be added to the revised caption.

27. "Given that detail of these regions comes in subsequent paragraphs, I'd reccomend changing this to a broader statement of motivation - i.e. targeted regions with well-constrained histories. Some more specific issues are teased here (e.g. alteration), but without key citations." (lines 129-133) Agreed, these lines will be edited in the revised manuscript.

28. "for which material are the sensitivity figures provided? These would be better

provided as cps/ppm (if a homogenous material)." (table 1) Sensitivity was measured on NIST SRM612. cps/ppm values will be given in the revised table.

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