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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.

James Darling (Referee)

james.darling@port.ac.uk

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General comments

The manuscript presents new data from in-situ U-Pb isotopic analysis of epidote in a series of hydrothermal veins, using modified LA-ICP-MS protocols. The method and results show great untapped potential for epidote (mineral) geochronology, building upon previous studies of allanite (REE-rich epidote supergroup mineral). Given the occurrence of epidote in a variety of important geological settings, the developments have great potential to improve the geochronology of crustal processes.

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Discussion paper

The manuscript documents an approach to correcting laser induced elemental fractionation using an allanite primary reference material. This shows excellent promise, and the resulting ages determined for epidotes in vein samples seem geologically reasonable. The manuscript is generally well-written and supported by some useful figures and tables (although there is room for improvement). Overall, I consider that the manuscript will be very well suited to Geochronology, following some modifications.

I have made a number of specific comments below that are presented in order of reading through the text. These can be broadly grouped into three areas that need some consideration:

(1) The documentation of downhole fractionation (DF) correction and error propagation needs to be clarified and expanded upon. Please see comments below that highlight inconsistencies between the text and Figures relating to DF corrected data, and which require a more balanced discussion of results.

(2) There are subtleties in the Grimsel-1 data that have not been discussed in the text, and may have significant implications for the interpretation of epidote ages in veins with complex histories. Please see comments listed below.

(3) Greater clarity is needed on the distinction on epidote (mineral) versus epidote group/supergroup minerals. This is particularly highlighted by the overlap and comparison with studies of allanite (REE-rich monoclinic epidote). The novely here is specifically in measurement of epidote (mineral), although solid-solution with clinozoisite should be acknowledged. This is particularly important given that chemical data (e.g. Al, REE, Fe) to demonstrate near end-member compositions has not been measured for the studied grains. Please see suggestions listed below.

Specific comments:

Lines 44-51: 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 v.

high REE+Th contents (i.e. "allanite")

Lines 45-46: epidote supergroup minerals can have wt. % levels of Th (i.e. allanite)

Lines 58-60: 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 99-103: 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 107-110: 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 115-118: 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 117-121: 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 215-220: detail of the DF corrections applied is missing here. How was DF modelled and corrected in Iolite?

Lines 224-226: 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 229-234: Please summarize here or in Table 3 the effect on precision of anchoring the 207Pb/206Pbc.

Section 4.1: 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.

Lines 324-345: As above, how was DF corrected in iolite? I've not seen details documented anywhere as yet (function used?).

Section 4.2 & Figure 4: 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.

Figure 5: 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?

Data for Grimsel 1, lines 388-398: 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?

Lines 466-467: 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 467-470: 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.

Section 5.3: 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 repetitive discussion.

Section 5.4: 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.

Lines 523-529: 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 545-555: 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....

Other technical suggestions:

Abstract, line 8: should read 238U (rather than 283U)

Abstract, lines 14-15: 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 20-21: 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

Lines 80-84: Need to split this into two sentences.

Line 93: minerals

Lines 83-96: there 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).

Figure 6 caption: there are two (b)s and no (c) listed

Figure 7 caption: what did the MatLab script do?

Lines 129-133: 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.

Table 1: for which material are the sensitivity figures provided? These would be better provided as cps/ppm (if a homogenous material).

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