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Interactive comment on "Direct U-Pb dating of carbonates from micron scale fsLA-ICPMS images using robust regression" *by* Guilhem Hoareau et al.

Anonymous Referee #1

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The paper by Hoareau et al. presents a new approach to U-Pb LA-ICP-MS dating of carbonates that uses a mapping strategy in combination with robust regression of pixel U-Pb ratios. The authors suggest the direct plotting of pixel values into isochron diagrams as a simple approach that allows easy visual access of data quality and can be applied in combination with pixel filtering or pixel colocalization. Image-guided or image based approaches to LA-ICP-MS dating of carbonate clearly have the advantage that some certainty about genetic homogeneity (or heterogeneity) of a sample can be gained. However, to collect a set of masses that are indicative of inclusions, alteration, or different generations of carbonate minerals in general requires a fast-scanning ICP-MS instrument. The analytical setup used to acquire the data for the submitted study

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is not capable of fast mass scanning and thus no chemical information in addition to U-Th-Pb isotope data was collected. In order to still test for age homogeneity of the mapped portion of the sample, a pixel value colocalization approach is used. This allows to obtain information on the location and distribution of pixels representing outliers identified by plotting U-Pb data in isochron diagrams and to draw subsets of the data for testing equivalence of the results.

As advance in instrumentation and software allows or even requires exploring new strategies for data acquisition and processing, the presented approach seems to be a good addition to the methods currently employed. I am, however, not a statistician and can therefore not judge whether the statistical base is appropriately chosen and correctly applied to the presented workflow. The manuscript is mostly clearly structured and written but needs clarification in several points. The English language may need some polishing too.

In the current version of the manuscript there is a lack of clarity on (1) how (or if) the data processing protocol deals with correction for instrumental drift, (2) how many NIST612 analyses are used for pixel ratio normalization (section 2.3.2; just the NIST analyses directly preceding and following that of the respective sample or those of the entire analytical session? And if the latter whether or not any excess scatter of the background- [and drift-?] corrected isotope ratios was observed) and (3) how the correction for radiogenic 208Pb from in-situ Th decay in Th-bearing samples is applied for the use of common 208Pb in the respective isochron plots. This should be clarified.

The identification of outlier pixel locations by colocalization is an attempt to data filtering that is not always efficient or successful. Apart from the usual "stray values" it may detect areas with low U and/or Pb concentrations where large scatter can exist due to insufficient counting statistics. Such scatter is inherent at very low ion signals and does not always justify exclusion of the data (key words: limit of detection, limit of quantification). The colocalization may also be successful in identifying areas with U loss (when surrounded by areas with pristine U-Pb systematics), where highly radiogenic

Pb isotope compositions at low 238U/206Pb would occur. The colocalization technique is, however, likely to fail in a case where different types/generations of carbonate minerals yield data point arrays that are intersecting each other in a small angle resulting in largely overlapping data point arrays. Please see comments to sections 3.1.4 and 3.2.2 for further explanation.

The lack of reported (numerical) data is also an issue. According to their data policy the journal requires a statement on where the data underlying a study can be found. Although the study presents/uses new data, there are no data submitted with the ms and a download link or a statement on data availability are missing. The approach presented in the study is new and associated data tables would be huge when choosing a format that would allow the reviewer/reader to plot and play with the data. Yet for potential further review and the case the manuscript is accepted for publication the authors should come up with an idea on data reporting and make the data accessible (Raw data files? Fully processed numerical pixel data? At the very least fully processed numerical values for sets obtained by discretization?...).

Specific comments

Abstract: Reference citations are normally avoided in the abstract.

1. Introduction:

first paragraph - the authors may want to clarify that the very good spatial resolution allows to detect and exploit sub-millimetre scale heterogeneities in U and initial Pb concentration

second paragraph - "...spot ablations of sizes close to 100 μm..." this statement is too imprecise; my own quick literature survey revealed that spot diameters range at least from 80 to 235μm depending on lab and U concentration of the samples. The actual range of spot diameters should be used here and a few citations can be added to give somewhat more credit to previous work in LA-ICPMS U-Pb carbonate dating.

third paragraph (from line 48) - it is not only detrital contamination that can be revealed by additional minor and trace element mapping but also alteration zones and different types or generations of carbonate minerals

2.2.2 from Line 116: (i) lines of 50μm width separated by 100μm distance - this is confusing as it would leave 50 or 150μm wide gaps between lines but Fig. S2 does not suggest there are gaps. Please rephrase. from Line 123: (ii) "...lines of 25μm width, separated by a distance of 25μm..." - again is this the spacing required by the "spot size" or are there 25μm gaps between the lines that are not ablated (Fig. 1 suggests the former) from Line 128: is the preablation (and second map) run directly over the previous screening map or is the sample repolished between screening and dating experiments? Line 130: the reference age of WC-1 is here given with 254.4 $\pm$ 7 Ma while Table 7.1 quotes 254.4 $\pm$ 6 Ma. Why not just use the original age of 254.4$\pm$6.4 Ma given by Roberts et al. (2017) for WC-1.

2.3.2 Lines 148/149 " The standard error (i.e., standard deviation of the mean) for each ratio was also calculated from the standard deviation which is an output of the function." - is this referring to NIST612 analyses? Line 153 - was an uncertainty applied when anchoring the regression? Roberts et al. (2017) give 0.85$\pm$0.04 for WC-1.

2.3.4 last sentence: The long-term excess variance cannot be derived from the primary reference material. Instead a quality control material (such as Duff Brown) should be used to assess this parameter.

2.3.5 - Residual Standard Error - A short statement on the range of acceptable RSE for different signal intensities could be given as dispersion is not only ruled by age homogeneity of the sample but also by counting statistics. - discretizing of pixels into sets by increasing 238U/206Pb ratios - what are acceptable values for d-MSWD? And wouldn't it be more appropriate to group the pixels into sets along the regression line rather than along the x-axis (i.e. 238U/206Pb) as the data points are scattered in both the x- and y-directions

2.3.6 Lines 209/210: "...not necessarily more accurate..." - shouldn't this read "not necessarily more precise"?

3.1 "... This is due to Pb0 values lower than that calculated from data of Hill et al. (2016) (0.738 $\pm$ 0.01, 1s). The discrepancy between both values is explained by the high 238U/206Pb ratio of the sample (typically 60-70) that prevents a precise determination of the common lead value. ..." It is not the high 238U/206Pb ratio or the low 207Pb/206Pb intercept itself but rather the lack of spread of the data points along a linear array which results in a poorly defined slope of the regression line and thus in imprecise and inaccurate values for both intercepts. Please clarify. Also an uncertainty for the initial 207Pb/206Pb composition of Duff Brown is quoted but anchoring is done without uncertainty as suggested by Fig. 2.

3.1.2 Line 227: "...large variation in the U/Pb ratios and a large amount of U..." - both parameters could be specified by giving the approx. range of U/Pb ratios and an approximate U concentration or the range of U concentration in brackets Lines 233-235:" This high precision can be related to the very good visual and statistical parameters calculated for this regression (good point alignment, very low RSE, and low d-MSWD..." - again the values could be given here rather than the narrative description of these values (also applies to further sections)

3.1.4 The pixel data show a lot more scatter around the regression line than the error ellipses of the spot data, i.e. the band in which the pixel data fall is much wider than a band covering the scattered (!) ellipses. This is not surprising but may be a problem. While spots were likely placed in a way not overlapping different textures (and thus error ellipses reflect the heterogeneity of the sample), the maps include all textural components and the pixel data represent a mixture of these different components. If there are small variations in ages and/or common Pb compositions for the different textural components this would not be obvious from plotting the pixel data as the different data point arrays are largely overlapping and may be intersecting each other in a small angle. The colocalization can be useful to locate areas that are rather heavily

affected by for instance U loss but will not necessarily be able to detect subtle differences in U-Pb systematics that result in slightly different slopes and intercepts of the regression lines of different components within the sample. One possibility to test for homogeneity might be dividing the map in squares/tiles with a size of a certain number of pixels (e.g., 125 x 130μm or corresponding to 20s) and to then check the alignment of the resulting ellipses. This is just one thing that could be tried but I don't know if this is feasible with the software used.

3.2.1 Line 284: "more precise" rather than "more accurate"? It looks like about half of the data for cement C2 are squandered and not used for age calculation when selecting a rectangular area...

3.2.2 From the description in the text and the caption of Figure 7 it is not clear to me which pixels were actually used for age calculation. The outlined area in the top left corner of the maps in Figure 7 does however seem to have very low U and Pb concentrations and larger deviations of such data points from the regression line can be expected just from counting statistics.

There seems to be an accident with the numbering of the sections as 3.2.2 is followed by 5.

5.1 Lines 309/310: "If not, the operator must remain attentive to the quality of the data, by checking the scattering of the pixels around the regression lines and the possible presence of phase mixtures." - this may not be enough (see comment to section 3.1.4) Lines 311/312: "The use of a colocalization approach as presented in our study is an efficient way to carry out this careful study of the spatial distribution of the furthest pixel values from the regression line." - see comments to sections 3.1.4 and 3.2.2. The values furthest away from the regression line are likely not too indicative of sample homogeneity/heterogeneity but often represent "true outliers" that cannot be related to age homogeneity in the sample. Line 322: "... maps can be built directly on thin sections (work of Drost et al., 2018) or on thick sections (this work)..." - The use of

thin sections (in the actual meaning, i.e. $\sim$25μm thickness) for high repetition rate mapping experiments in carbonates is dangerous due to preparation-related potential local deviations from the targeted thickness of the thin section and due to potentially heterogeneous sample material that may result in different local ablation rates. The experiments of the presented study resulted in 25 to 35μm depths confirming this and Drost et al. 2018 state the use of a "...polished rock slab of the sample..." instead of a thin section. The sentence should be rephrased avoiding to encourage the use of thin sections.

7.1 Analytical conditions table: There is a comment that "Ages in the data table are quoted at 95% absolute ..." I could not find a data table in the manuscript or supplement.

Figure captions (Figs. 2 - 5, 7): is "pseudo-ellipses" the intended term?

Figures: Fonts in figures appear to be too small.

Figure S2: which element or isotope ratio is shown on the maps?

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