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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.

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RC2: "This is an interesting manuscript that shows the first application of a fs LA system to U-Pb dating of carbonates. While a method using an imaging approach similar as in Drost 2018 is used, a direct comparison including differences and improvements is only partly given and should be improved. To show that the robust regression works similar or better than the approach by Drost 2018, a direct comparison on the same data set using both approaches should be given."

Thank you for your comments. We have followed your recommendations by asking Kerstin Drost (which is warmly thanked) 2 sets of data corresponding to samples presented in Drost et al (2018) (JS4) and Roberts et al (2019) (BM18). Sample JS4 is characterized by high U concentrations (mean ca. 10 ppm) allowing precise ages to be obtained by the method of Drost et al. (2018) (297.8 $\pm$ 3.3 Ma, 297.2 $\pm$ 3.9 Ma, and 297.0 $\pm$ 2.9 Ma for the TW, 86TW and isochron diagrams, respectively). Those calculated with the robust regression method are similar to the previous within uncertainties (298.9 $\pm$ 3.4 Ma, 297.0 $\pm$ 3.4 Ma, and 300.8 $\pm$ 2.8 Ma for the TW, 86TW and isochron diagrams, respectively), with similar uncertainties and very good statistics (RSE < 5.5% of the y-intercept (see responses to the first reviewer), and d-MSWD $\leq$ 1). Note that to concur with results given by Drost et al. (2018), systematic uncertainties are not considered. Adding them leads to final age uncertainties above 8 Ma. For sample BM18, the low U and Pb concentrations (mean of ca. 200 pb and ca. 7 ppb, respectively) are logically associated with a large dispersion of U-Pb and Pb-Pb isotope ratios. The age obtained with the image-based approach as presented in Roberts et al (2019) (61.0 $\pm$ 1.7 Ma in the TW space) and with LA-ICP-MS spot analysis (59.5 $\pm$ 2.7 Ma; Beaudoin et al., 2018) could not be reproduced with our method. This is due to the presence of pixels with high 238U/206Pb acting as leverage points for the robust regression in the TW and 86TW diagrams. When systematic uncertainties similar to those of Beaudoin et al (2018) are considered, the ages are 46.9 $\pm$ 2.8 Ma and 48.4 $\pm$ 2.5 Ma for the TW and 86TW diagrams, respectively, more than 10 Ma younger than the expected one. For the isochron diagram, the age of 60.9 $\pm$ 2.1 Ma is similar to the expected age. Added to high RSE values (> 10% of the y-intercept value, see responses to the first reviewer), and d-MSWD values ranging from 2.5 to 4.9, these variable ages would lead us to consider this analysis as unreliable and to reject it. In order to improve our approach and get closer to the reference age, we have implemented the possibility to weight the pixel values used in the robust regression (weighted robust regression is made possible with the 'lmrob' library). Our choice is to attribute a weight to each pixel based on the density of pixels in the considered diagram. In the case of a large dispersion of data (especially related to counting statistics, even for a sample of homogeneous age), it is expected that the majority of points will still be clustered along the isochron (i.e., higher density of points). Assigning more weight to these points should limit the impact of leverage points. Density in the 2D space (and so pixel weight) was estimated by a gaussian kernel density estimate (KDE), whose bandwidth is estimated by the Scott's Rule (Scott, 1992). Using this approach to the anomalous ages (TW and TW86) gives values similar within uncertainties to that of Beaudoin et al. (2018), but still centered towards younger ages (54.4 $\pm$ 2.6 Ma and 55.0 $\pm$ 2.5 Ma for the TW and 86TW diagrams, respectively). The ages obtained with the 3 diagrams are not similar within uncertainty, which again would lead us to reject the analysis or, as they are close, to consider that the real age is likely comprised between 52 Ma and 63 Ma. We have tentatively reproduced the approach of Drost et al. (2018) by discretizing pixel ratio values and sorting them based on the 235/207 ratio (21 subsets). In the TW diagram, we obtain an age of 60.0 $\pm$ 2.8 Ma (MSWD = 0.95; with systematic uncertainties including long-term uncertainty), which is slightly younger than the value presented in Roberts et al. (2019). Making the same calculation for TW86 and isochron diagrams (not given in Roberts et al., 2019) gives values of 55.6 $\pm$ 2.9 Ma (MSWD = 1) and 60.1 $\pm$ 6.4 Ma (MSWD = 0.51), respectively. The 3 ages are centered between 55 Ma and 60 Ma, similar to those obtained with our approach. However, they are similar within uncertainties, which is not the case with the robust regression. Finally, we note that for the image-based dating obtained by Roberts et al. (2019) (TW diagram), the value of Pb0 (ca. 0.7) is significantly higher than that expected based on the spot analyses (ca. 0.59; Beaudoin et al., 2018)). The latter is, in contrast, almost identical to that obtained by weighted robust regression (ca. 0.57). For this sample of low U and Pb concentration, the approach of Drost et al. (2018) thus gives better results than the one presented in our study in terms of age, despite "wrong" y-intercept and slope values of the regression line (at least in the TW plot). We propose to discuss these differences in the revised manuscript, and to remind that for such kind of samples, spot-based dating should be preferred to image-based dating.

D.W. Scott, “Multivariate Density Estimation: Theory, Practice, and Visualization”, John Wiley & Sons, New York, Chicester, 1992.

RC2: "Generally, the improvements and new findings compared to existing and published methods should be more emphasised, including the use of fs LA, its possibility of high repetition rates, fast scanning, and the ease of use of the robust regression of individual points."

The only studies devoted to U-Pb dating of carbonates from isotopic images are those of Drost et al (2018), Roberts et al (2019) and this work. The comparison between the approaches will be largely addressed in the revised version (see previous response). The advantages of the isotope imaging method compared to spot analyses will be discussed in more detail in section 5.1. While for the majority of the examples presented in our study (Duff Brown, BH14, PXG20-1, PXG32-2) we show that the ages obtained by imaging are identical with spot analyses (both in terms of value and uncertainty), the example of the BM18 sample, which will be added to the manuscript, shows that in the case of very low concentrations of U and Pb the spot approach seems to be more efficient. We have deliberately not deeply discussed the possible advantages / disadvantages related to the use of a high repetition rate fs laser, as this is not the aim of this study. The major advantage is the small beam size, which allows to build images of reduced size if necessary (pixels 12 x 25 μm), as already explained in the text. Instead, we wish to emphasize the ease of use of the robust regression dating approach, which can be used whatever the device used for image acquisition.

RC2: "Please provide the "raw" data of your images so that the interested scientist can look and play with the data themselves"

This will be done (see answer to R1)

RC2: "Please be consistent and always us ICP-MS or ICPMS. Abstract: Quite a few carbonate ages are published using quadrupole ICP-MS, I suggest to generally talk about ICP-MS in the abstract."

The required corrections will be done.

RC2: “Line 57-58:” Additional examples of the interest of this new approach are provided in Roberts et al. (2019).” This sentence does not fit here.”

It will be removed.

RC2: “Line 87: Please clarify where the age with poor statistics is coming from.”

The age was obtained in our laboratory by LA-ICP-MS spot analysis with the methodology detailed in the Supplementary material. It will be clarified in the text.

RC2: “Line 105: mixing of He aerosol flow with Ar “in” the ICP-MS ? Please be more precise.”

The Argon, nitrogen and helium are all entering a twister spray chamber before reaching the plasma. This spray chamber has been modified by adding an additional inlet for the introduction of helium (transporting the ablated aerosol). It has been placed at the very top of the spray chamber and do not enter the chamber itself. We propose to add more detail to the text: “To improve sensitivity, 10 mL.min-1 of nitrogen was added to the twister spray chamber of the ICPMS via a tangential inlet while helium flow was introduced via another tangential inlet located at the very top of the spray chamber.”

RC2: “Line 110: I do not think it is relevant that the ICP-MS used is a HR instrument, but a sector field.”

OK.

RC2: “Line 116: The first image: No pre-cleaning pulses? How do you recognise surface Pb contamination?”

The images were done without pre-cleaning. Indeed, these images are only semi-quantitative, and aim to locate areas with both high U/Pb ratios and some spread in the ratios (see below).

RC2: “Line 132: If you apply the robust regression that puts the lowest weight to the outliers, why is in your procedure a second step necessary rejecting 2.5% outliers?

What is the difference to the results without rejection?”

We agree. This step is not really justified since the results obtained with and without outliers are almost similar. To follow your recommendations, we have decided to remove this step.

RC2: “Line 141: Each pixel of the image consists of 8 measurements (average) it should then be possible to calculate an uncertainty, and a different regression approach might be possible for comparison with the robust regression presented here.”

The uncertainties (standard error) obtained on only 8 pixels are too high to make reliable York type regressions. Instead, we propose to perform regressions on averages and uncertainties calculated by separating the maps into several sub-maps, following the recommendations of the first reviewer. The ages obtained agree with those from the robust regression, but with much higher uncertainties.

RC2: “Do you do the first and second image on the same day, same sequence?”

The first image is used only as a guide to select the area most favorable for dating. They are usually not necessarily performed on the same sequence, neither on the same day.

RC2: “How long does it take to analyse image 1 get the image as presented in figure S2?”

We are not sure to understand the question. The time shown in figure S2 for each image corresponds to the analysis time required to obtain that image. The treatment to plot the image from raw data consists in a few lines of code, so it is done in less than a minute.

RC2: “What is the criterion to select the region for image 2? (I would guess highest U/Pb variability or highest U concentration). Based on figure S2 this is not clear or rather random especially for Sample ETC2 as the image 2 is outside image 1, Why?”

The criterion used are at the same time the presence of high U/Pb ratios and large variations in U/Pb ratios, on an area of size corresponding to images used for dating. This is not random. For sample ETC2, the wrong location is due to a mistake of the operator during the analytical session. We decided to present the map anyway, since despite this error the age obtained is satisfactory.

RC2: “Drift correction with RM measured only every 38 to 76 minutes? No Drift correction for the U/Pb ratio? Please describe your approach in drift correction and its influence on uncertainties in more detail.”

There seems to be some confusion. The times shown in figure S2 correspond to the images used to identify areas suitable for dating. No standards are used to obtain these maps. Standards are used for the second maps, which are obtained in 19 to 38 minutes. For the latter, yes, the standards are analysed before and after the maps, as detailed in the discussion with reviewer 1. The standards are used for normalization of the Pb/Pb ratios, and drift correction of the U/Pb ratios, by bracketing. More details will be given in section 2.3. as also requested by the other reviewer.

RC2: “All figures with the robust regression have a white to blue, 0.x-1 colour scheme indicated on the right (I assume the weight as described in section 2.3.3?), but nowhere explained what it means. There are also open circle symbols likely the outliers that are not described. Please give this information either directly in the figures, or the figure caption, or leave it and just have points. Light blue to white points are hardly visible on white background.”

The color scale has been changed. The key (weights) will be added. The problem of the open circle symbols no longer arises because they were linked to the rejection of outliers, which is no longer carried out.

RC2: “Section 7.1 Please give the sensitivity of your instrument as % of # ions detected of # of atoms ablated, e.g. for a volume measured crater in NIST 610 and a measurement of U only.”

The percentage of ions detected with regard to atoms ablated is ca. 0.04% for U, as calculated with NIST 612 with the ICPMS method used for the dating map (comprising 6 isotopes).

RC2: "Please mention what kind of ablation cell is used, single volume, 2 volume, manufacturer, size, shape etc."

The laser ablation system is equipped with a home-made (home-designed) two volumes ablation cell. The large cell has a rectangular shape and a volume of 11.25 cm3 (75 x 25 x 6 mm size) while the small one, placed above the sample is of 10 mm diameter. These details will be added to the manuscript.

RC2: "What is the possible sample throughput of your system per day with the described method?"

The sample throughput is about 4 to 6 samples / day for the unknowns. It would certainly be higher with a more adapted equipment. We want to emphasize again that our work is aimed at highlighting the robust regression treatment, more than the devices used for the analyses.

RC2: "Out of curiosity, what kind of cones (Jet sampler and H or X skimmer) do you use in combination with the Jet Interface of your Element XR? (this does not need to be part of the manuscript)"

We use Ni-jet version with a Ni X-version skimmer.

RC2: "figure S2: mn should be min. Please indicate what is plotted either in the figure itself or the caption (238U/206Pb)?"

The requested modifications will be made.

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