Geochronology Discuss.,
https://doi.org/10.5194/gchron-2019-20-AC1, 2020

Interactive comment on "New analytical and data evaluation protocols to improve the reliability of U-Pb LA-ICP-MS carbonate dating" *by* Marcel Guillong et al.

Marcel Guillong et al.

guillong@erdw.ethz.ch

Received and published: 6 April 2020

Thank you for the comments and suggestions that helped to improve the manuscript. Please find below some answers, comments and findings.

72-73: We completely agree that downhole fractionation is an important effect to be considered in U-Pb dating, which has been shown in many details in the case of zircon, and that it is necessary to be extremely careful with its correction to get the best possible accuracy. However, we observed in the case of carbonate U-Pb dating some differences:

Printer-friendly version

Discussion paper

1. Downhole fractionation of NIST 614 and any carbonate material is not comparable, therefore, any attempt to correct a carbonate LA signals using NIST 614 can introduce systematic errors. Even the downhole fractionation trend between different carbonates can be different Fig. RA1

2. Due to the variability of different carbonate minerals and textures, the ablation rate can vary as is shown in the manuscript. Therefore, an attempt to match integration intervals between standard and samples will unfortunately not be perfect as it might be different with respect to downhole fractionation.

3. We agree that if all carbonates showed the same downhole fractionation pattern the approach to get best accuracy is to use exactly the same interval, but due to heterogeneity in ablation rate, within-run variations in initial Pb, U content, and age variations this is hardly possible: a comparison for one piece of JT (10 ablations) is presented comparing total integration with selective and multiple integrations. Fig. RA2

4. If there are high- and low initial Pb zones within a single ablation (which is not uncommon), the total interval will show a large uncertainty with little contribution to a well defined isochron. Two separate integration intervals for high initial Pb and low initial Pb will result in 2 measurement points contributing to a better-defined Isochron, even if the matrix/downhole correction with the total interval from the reference material will add a systematic offset. However, we assume that the variability of initial Pb is randomly distributed from a crater to another and therefore the possible offset is averaged out. Fig. RA2. This might become a problem when the "initial" Pb is mainly at the beginning of the signal due to surface contamination. All precaution should be taken to minimize surface contamination (careful cleaning and pre-ablation).

5. One possible solution would be that only signals where there is minimal variation within the ablation for initial Pb are considered, but then quite a lot of ablations will have to be discarded.

6. We agree on the referee's point that the "adjustments were random enough not to

make enough of a difference in the final age”. We also agree that it can be possible by selecting only later parts of the signal, the final age will get older respectively younger when only the first parts of the signal are selected. However, the new data of JT, for which we systematically investigated this effect, does not show this behaviour, although data on e.g WC-1 with a clear increasing downhole fractionation trend (Fig RA1) will certainly show this effect. Fig. RA3

7. Figure RA4: shows the downhole trend of WC-1 for different aspect ratios (mean of n>15 signals) both comparing vs time (A) and vs the estimated aspect ratio (B). This figure shows that up to an aspect ratio of 0.2-0.3 no clear downhole trend is observed and only for higher aspect ratios the Pb/U increases significantly.

Therefore, we changed the description accordingly: “The selection of different integration intervals along a single hole ablation can introduce systematic offsets if not randomly distributed due to different amounts of downhole fractionation between RM and sample if there is significant amount of downhole fractionation in either the RM and/or the sample. Best practice is to use as good as possible the same integration intervals with respect to crater shape for both the RM and the sample. As is demonstrated, it is likely that random variability of downhole fractionation, ablation rate, distribution of initial Pb etc. would anyway mitigate the offset potentially introduced. This potentially introduced offset would anyway be diluted in the propagation of the systematic uncertainties, especially since the long term excess variance of secondary RM could precisely result from this.

We improved the manuscript according to some detailed comments.

143: The rather controversially comment “as sometimes done in carbonate U-Pb dating by LA-ICP-MS” has its origin in both personal communications and some unfortunately rather vague descriptions of analytical methods in some publications (like e.g. Nuriel et al., 2017: “either 85 or 110 micron spot size” but no clear statement about whether this is for different sessions or a single one; https://doi.org/10.1130/G38903.1). Therefore, it is of course clearly not suggested in literature to use different crater sizes until now, but this may not prevent users to do so, so we felt like this was important to stress out. To temper this, we adjusted the statement, and can recommend to use different spot sizes and repetition rate as long as the aspect ratio is the same as the reference material.

Figure 4: We adjusted the Y-axis to offset from the ref. value. The associated uncertainties for both the age and the aspect ratio mismatch are large. Especially, the uncertainty of the aspect ratio mismatch relative to the RM is difficult to quantify. Indeed, these values result from a combination of estimations based on the number of pulses and an average ablation rate for this sample, itself based on measurements made for some (but not all) craters in some (but not all) sessions. We think that measuring the depth of each individual crater as precisely as possible would be a considerable amount of work considering the small influence that it would have on the final results. Therefore, we do not give an uncertainty on the x value and also refrain from calculating an uncertainty on the slope. Based on the new slopes, we think they are equal within uncertainty.

Figure 4 is also meant to show the general effect observed and described in this manuscript that with changes of the crater geometry you likely get significant age offsets. However, the ablation rate of the carbonates is extremely variable (as shown in Figure 5) and can vary both from spot to spot of the sample sample, as we occasionally observed. The figure qualitatively shows that the described effect is present, and that with different aspect ratios an offset is introduced.

What the referee 1 suggests is in the end a perfect matrix matching between RM and sample, which considering all the sources of uncertainty above, is in our opinion not possible. What we can suggest is therefore a reasonable approach to get as accurate results as possible for many interesting applications with the presented approach.

To be able to adjust the crater size is an advantage that makes LA-ICP-MS the method of choice for many applications that we would not sacrifice this versatility, but obviously care has to be taken. If the grain size of a sample is highly variable we like to apply different crater sizes to get trace element content for low concentration with larger spot size and good reproducibility for higher trace elements with many replicates of small craters. In the end there have to be some compromises and we think that in the manuscript we show a way to use different sample sizes without sacrificing the accuracy too much by adjusting as good as possible the crater geometry. We think the dependence of the uncertainty on the signal intensity is well shown in literature and with larger craters a higher ablation rate more sensitivity gives smaller uncertainty.

In the end, we are confident that using the excess uncertainty as recommended in this manuscript would anyway cover the uncertainty associated with the differences between RM and most samples, including differences in downhole fractionation, ablation rate, integration intervals, etc. – as long as the aspect ratio of the craters is kept similar and the whole analytical protocol is followed as good as possible.

Interactive comment on Geochronology Discuss., https://doi.org/10.5194/gchron-2019-20, 2020.

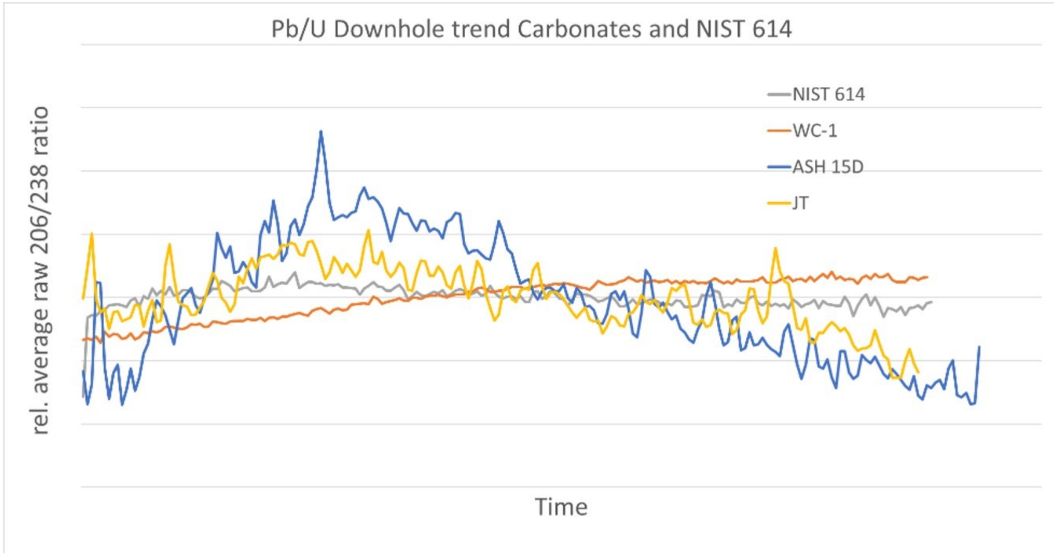

Fig. 1. Relative to the mean raw 206/238 ratio) downhole fractionation trend for 3 different Carbonates and NIST 614 showing no consistent trend, making a downhole fractionation correction of unknown samples

Printer-friendly version

Discussion paper

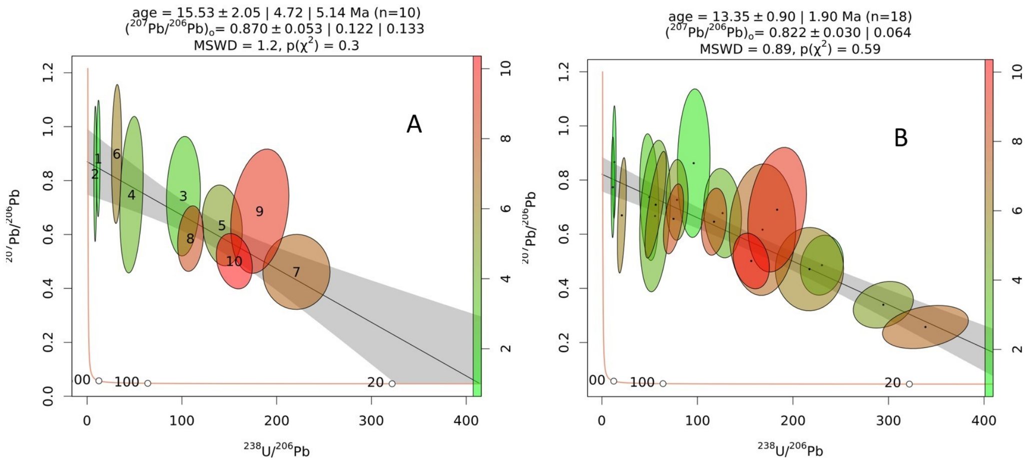

Fig. 2. Comparison of 10 JT ablation once integrated the whole signal (A) and once integrated to get max. spread of Pb/U ratios including multiple integration intervals per signal showing a clear improvement

Printer-friendly version

Discussion paper

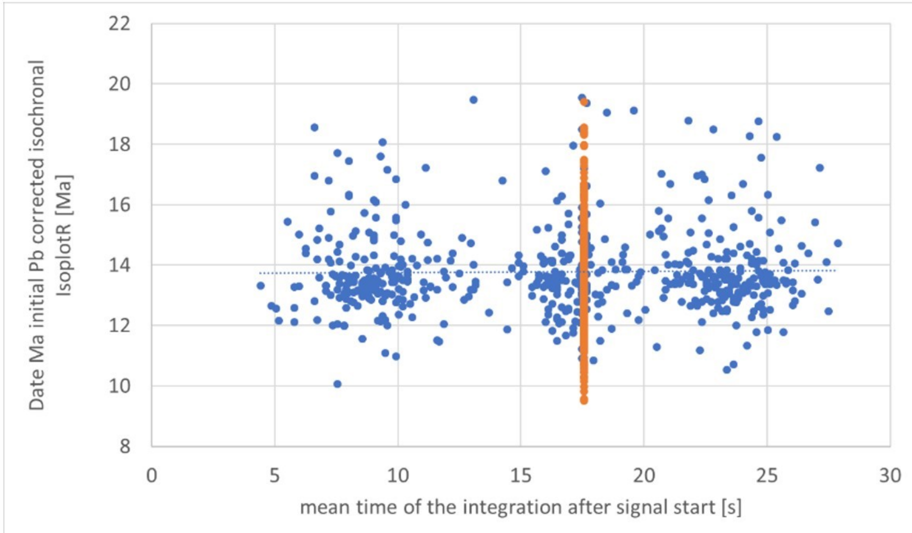

Fig. 3. Individual, isochronal initial Pb corrected JT ages vs. the mean time of integration after laser starts ablating. Blue points indicate selective integrations often the first part (around 8 seconds) an

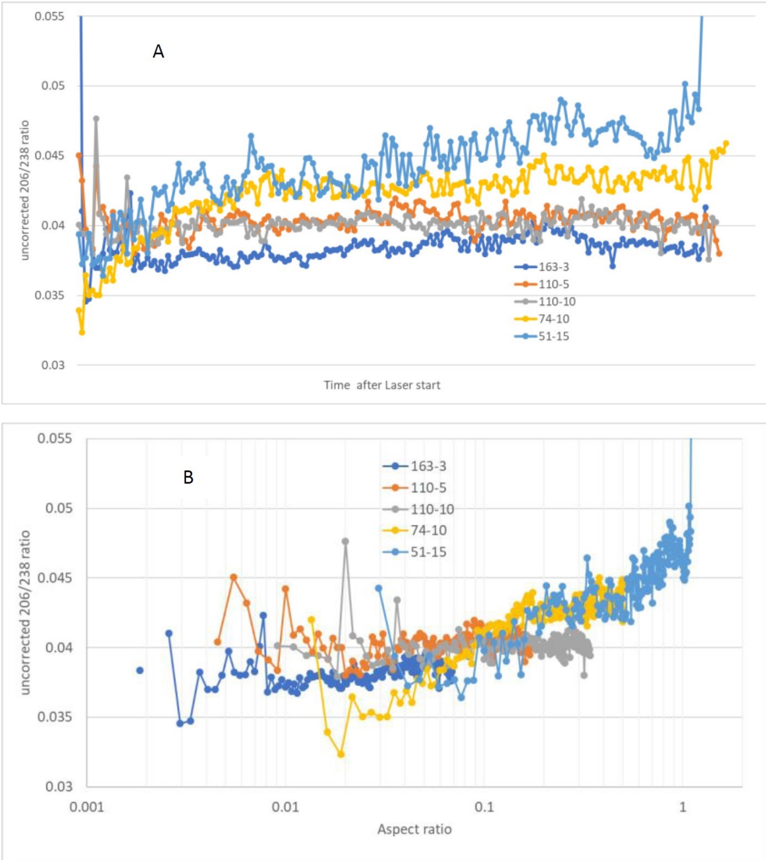

Fig. 4. The downhole fractionation trend of WC-1 for different aspect ratios (mean of n>15 signals, different crater sizes and repetition rate from 163 microns at 3 Hz to 51 microns and 15Hz) both comparing