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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.

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

Please also see also answers to RC 1 and 2:

Thank you for pointing out parts of the long and intensively discussed, investigated literature on inter element fractionation. We are well aware of the large amount of interesting and good literature about it, but we would not like to write a review manuscript on this topic so we kept the referencing and discussion to the necessary part, also with respect to the length of the manuscript. Additionally, we investigated downhole fractionation in carbonates, but no clear results emerged (e.g. Figure RA 1) or some investigations using the matrix matched synthetic reference material of pressed powder MACS-3 which is "completely useless for U/Pb dating of carbonates" due to heterogeneity and non-reproducible U-Pb fractionation behaviour.

We added some more detailed investigations on the JT samples and pieces available for distribution, including an image of all available pieces and results of 10 analyses on all possible aliquots that can be distributed. Part of our work over the past couple of years consisted in investigating the suitability of other possible secondary RM, but so far all tested materials but JT were unsuitable.

We added a whole new chapter to the Electronic appendix describing the available pieces of JT in more detail. We agree that JT is both of limited supply and use for low sensitivity ICP-MS, however we think that it is with all the limitations a valuable addition to the collection of possible RM and usable as VRM for some laboratories.

Line 72: We now state: "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."

Line 140-145. See answer to RC1 about this topic.

Section 2.33

1) U heterogeneity is often at a smaller scale than the pit depth/diameter. Such that a high U zone in the pre-screening may turn out to be low U for the next 30 seconds of ablation (and vice versa). We agree, but the opposite is also true: a low U signal during screening may have yielded a higher U signal if ablated longer. This is why we systematically ablate several screening spots per sample, to get an idea of not only the U and initial Pb contents, but also their variability. This fast pre-screening gives some first hints and indications of the possibility if the sample is datable or not, which saves a lot of spot programming and analytical time. From personal communications, we know that other laboratories apply similar strategies.

2) Chemical and physical heterogeneity can be large, such that the drill rate probably changes a lot during 30 secs of ablation, not just between different materials. Yes, we agree, as discussed earlier for replies to other referees. We believe that this is at least partly the reason for the larger excess uncertainties we obtain here for carbonate U-Pb dating, compared to zircon geochronology.

3) This two-step strategy would add a lot of time to the workflow. The extra time that this short test sequence costs is much less compared to the time lost if samples with very low U are present and not identified. So we would argue that on the long run, this two-step strategy saves time and resources.

4) How is the rep rate adjusted to exactly match the aspect ratio? – for a fixed focus point at the surface of the sample, drill rate is non-linear as you drill down such that exact estimation of depth is difficult. The rep rate is adjusted assuming equal ablation rate per pulse independent of the crater size and depth. Ablation rate variations due to laser focus are generally small in LA up to an aspect ratio of 1 (i.e. for most aspect ratios considered in this study and carbonate dating in general, for which large spot diameters are used), and likely more influenced by the sample properties (Horn, 2001).

5) Post ablation measurement of pits will also add significantly more time to the overall data workflow. Yes, we do not suggest doing this routinely and this would not be nec-

essary anyway if one follows our suggestion to match aspect ratios between RM and unknowns. The depth measurement was specifically performed here to evaluate the importance of the ablation rate and aspect ratios.

6) Applying the correction is not actually tested for some unknowns here, so we don't really know if this two-step strategy is going to be an overall improvement for heterogeneous materials. We assume that this comment is about the correction for similar aspect ratio, and if so, yes we do not show data for "heterogeneous" unknowns and only for Ash-15D and JT. Of course, we cannot exclude that strong heterogeneity in ablation rates for unknowns would result in age offsets. However, as discussed above (reply to reviewer 1) this effect is likely to be mitigated between different spots and matching as good as possible the aspect ratio of the unknowns to the RM is the best way to minimize it.

7) "A detailed study on how to best apply this correction if necessary is beyond the scope of this work. . ." – it would appear then that this is basically untested. The authors critically undermine their arguments in their final sentence of this section: "we suggest for a more robust data reduction to always use similar aspect ratios". I would argue that this is exactly what should have been done, and that the community needs to try and find more RMs with a range of U contents. What is beyond the scope of this manuscript is to present a method that includes a correction based on crater depth measurements post ablation. What is improving the data quality and versatility is to match the aspect ratio of the pre tested samples to the RM. Using this the amount of ablated material and intensity of U can be adjusted closer to that of the RM. As long as there are not more RM with matching U content and ablation behaviour are available this is in our opinion the best possibility to get best possible precision and accuracy. Additionally, the huge variability of U contents in carbonates, and the fact that we don't really know how high it is a priori is a good argument to for our approach. Matching aspect ratios, rather than spot diameters and U content with a series of RM, is much easier and more cost-/time-efficient at present and is the only option having only one

reliable primary RM (WC-1) in the community.

We rephrased to make this point clearer.

Section 2.5:

We rephrased this section to better reflect the information presented in Roberts et al. (2017) concerning the white zone, added the isochrone to the white part and the ages for comparison. "The plots in Roberts et al. (2017) demonstrate that the white Th-rich region analysed in their data is high in common lead, but that the data-points presented seem to be broadly of the right age. It would appear that the author's data shows that some of these altered regions are not the same age. However, rather than a different age being implied, this is just as likely to be variation due to open-system behaviour; an age might not be definable. So, WC-1 may be heterogeneous in age or homogeneous in age with white zones of alteration causing open system U-Pb behaviour in these zones. When this alteration occurred relative to the dated phase is not resolvable and could have occurred quickly after the formation age or sometime after."

We are convinced that the two phases (the dark and the white zones) show carbonate precipitation at two significantly different points in time / in the burial history of the Capitanian Reef Complex. The black zone (which is the regular part of WC-1 that should be used as RM) is composed of marine botryoidal cements (Roberts et al. 2017) while the white zone is composed of vein-like, more sparry cements (again showing two zonings of different luminosity as can be seen by cathodoluminescence microscopy) with sharp contacts to the surrounding botryoidal cements. If the difference in U-Pb between the botryoidal cements and the more sparry white cements would just be the result of open system behavior, the two cements would not show the difference in texture reflecting different ambient conditions during precipitation that we observe (e.g. crystal size, shape). Also, the U-Pb data of the younger (leached) phase would not define an isochron (which it more or less does, age 203 +/-7 Ma) but rather be random distributed towards younger ages. The larger scatter in the data of the white zone can

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potentially be explained as artefact due to mixture of the dark and white phases in the lower part of the ablation pits (the vein might be tilted) and by the fact that later-diagenetic phases like veins in our experience are commonly more noisy compared to WC-1. We therefore argue that WC-1 is heterogeneous in age. However, the white zones can easily be seen by cathodoluminescence (it has a very bright luminosity compared to the botryoidal cements) so that it is not a problem for the community to avoid the white zones.

Line 241: It is the offset of the average LA-ICP-MS age for ASH15-D compared to the ID-TIMS age. As the ID-TIMS results for ASH15 are not part of this manuscript but in (Nuriel et al., in prep.) and there is an offset observable in both Figure 2b and 4c, we do not ignore this but mention that there is this offset, and a possible explanation is given in the conclusion: "This offset cannot be explained completely by differences in ablation rate and may be an additional matrix effect to be investigated in detail in future work." This offset is already mentioned in the Abstract: "Additionally, a systematic offset to the ID-TIMS age of 2-3% was observed for ASH-15D but not for JT. This offset might be due to different ablation rates of ASH-15D compared to the primary RM or remaining matrix effects, even when chosen aspect ratios are similar."

We consider changing the title as suggested and present the data in a different light.

Attached is a file and table S3 that we would like to add to the electronic supplementary information of the main manuscript containing analyses of all the available parts of JT.

Please also note the supplement to this comment:
https://www.geochronology-discuss.net/gchron-2019-20/gchron-2019-20-AC3-supplement.zip

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

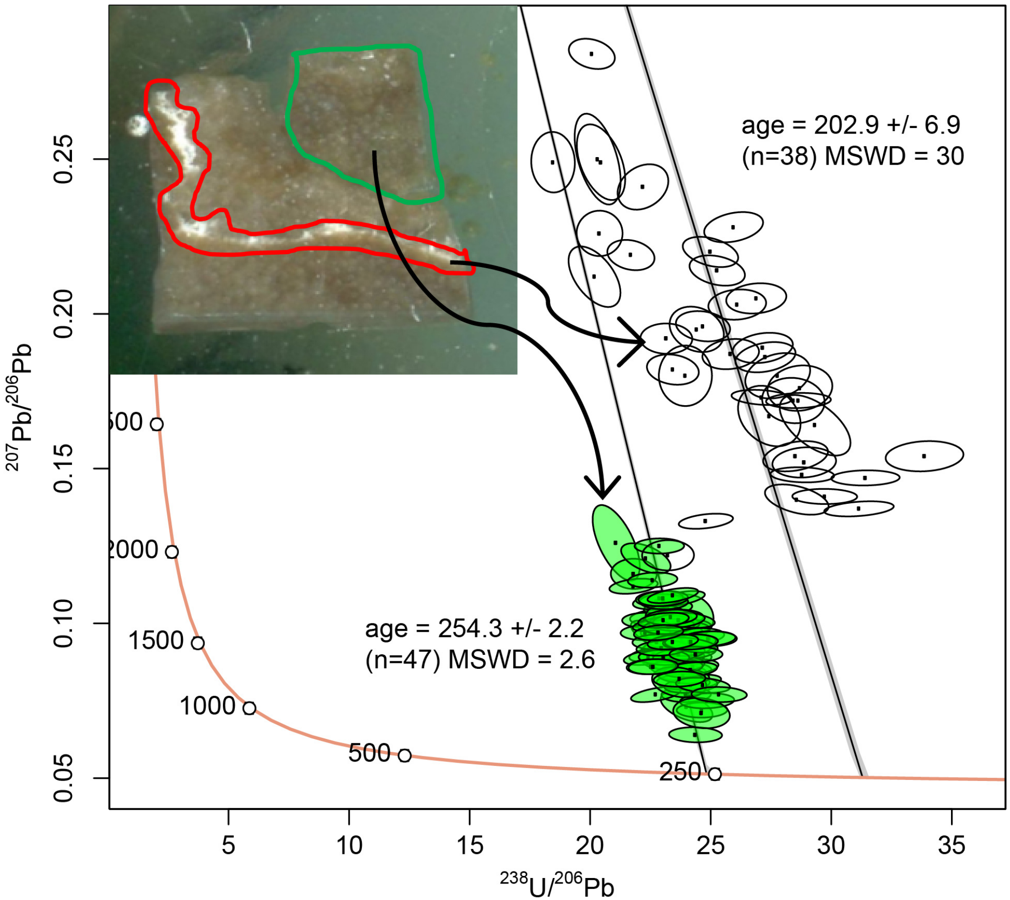

Fig. 1. Improved Fig. 7 from the manuscript showing the age difference between the regular part and the white vein-like, more sparry cements.