Geochronology Discuss.,
https://doi.org/10.5194/gchron-2019-20-SC1, 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.

Nick Roberts

nirob@bgs.ac.uk

Received and published: 9 March 2020

Review of Guillong et al

Firstly, this paper presents an important dataset that is of value to the community – a measurement of the potential matrix-effects when measuring U-Pb in carbonate materials. On its own, this would be a useful publication.

Secondly, the paper presents a potential new reference material for U-Pb carbonate geochronology. This is also much needed.

However, a lot of the paper discusses issues with matrix/ablation-matching, and there-

fore the description of the new JT RM is rather scant. How radiogenic is any one region of JT? If JT is distributed, will all aliquots have enough radiogenic lead, and enough spread in U/Pb ratios?

The paper has major flaws in both its presentation, and its message, but which can be very easily amended.

Firstly, using different spot sizes (and hence aspect ratios) for inter-element work, is not common practice within the community and I am not aware of it being advocated as good practice. Early in LA-ICP-MS development (particularly for zircon U-Pb geochronology) papers such as Mank & Mason (1999) and Horn et al. (2000) demonstrated that downhole fractionation affects the resultant U/Pb age, and that drill-rate and aspect ratio are the dominant control on the behaviour of downhole fractionation for any one material. Horn et al. (2000) did in fact demonstrate very broadly that calibration without external normalisation can be achieved. However, this method was soon surpassed (at least by most) by those that advocated matrix and ablation-condition matching (e.g. Jackson et al., 2004). Several other recent papers have tried to tackle ways of reducing inter-element fractionation in zircon U-Pb, e.g. Allen et al. (2012), Solari et al. (2015) and Marillo-Sialer et al. (2014). I do not question the knowledge of the authors on these issues, but the way the issue is presented in this current paper should be addressed to reflect the considerable work that has gone before in controlling and standardising inter-element fractionation during LA-ICP-MS, albeit for U-Pb most of it is through analysis of zircon rather than carbonate.

This paper provides a useful dataset building on the work that has been conducted on zircon regarding matrix-matching, and should be presented in that light. This study documents the scale of the matrix effects (in terms of downhole fractionation) of carbonate materials, and along with the potential new RM, these should be the key messages.

Line 43 – this should be: (e.g. Beaudoin et al., 2018), since many of the listed and not-listed papers (in the previous sentence) state the results from secondary RMs.

(Although technically these are not as yet 'RMs', but merely materials that have been analysed with isotope dilution methods in previous literature).

Line 72 – This line describes a process that has major implications for the accuracy of the data, if, certain precautions are not taken. If a suitable data reduction algorithm is used, that matches the same region of the standard as that of the sample – as in most Iolite U-Pb data reduction schemes, then the accuracy is largely going to be maintained (maybe a minor degradation in accuracy). If the analytical protocol produces a U/Pb profile with no measurable downhole fractionation, then this type of cutting up of the integration can be achieved fairly accurately also. However, the latter is normally only possible with very low aspect ratios or with rasters.

Section 1.4 If this paper is going to be the only paper that presents JT as a RM, then it is rather lacking in detail.

How much JT is available?

How homogeneous is the material chemically and physically?

The data are not dominated by radiogenic lead, but instead provide a spread in U/Pb ratios. This is favourable for generating a precise age, but, will any given 20 spots in one session provide a large spread in U/Pb. i.e. what is the scale of U/Pb heterogeneity across this material?

These factors have to be considered if the material is to be of use to the community. 207Pb counts in JT are presumably quite low. Therefore this material, like ASH15, may have limited use for the Q-ICP-MS community.

Section 2.2 This long-term variance seems reasonable, and about what I would expect based on my own and others general experience.

It is a pretty good validation of the method as a whole, given the overall heterogeneous nature of carbonates.

Line 140-145. "...as sometimes done in carbonate U-Pb dating by LA-ICP-MS". By whom? To my knowledge no one has ever stated this. It is certainly not 'normal' procedure. If it is something that people do, then they need to be more open about this in the description of their method and analytical protocol.

Section 2.3.2

It is a shame more dolomite types were not analysed. This is pending further work I guess, and would ideally involve a dolomite RM. Overall though, these data show some very useful quantification of the potential issues.

Section 2.3.3

"Strategies for matching aspect ratios"

This should just simply state – "match the RMs to the unknowns".

It may not be ideal to match the spot size, due to low U in calcite, but that is just par for the course, and a limitation of the method. Carbonates are a non-ideal U-Pb chronometer. "We suggest a two-step strategy to account for this issue..." This seems like a very time-consuming and problematic workaround:

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).

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.

3) This two-step strategy would add a lot of time to the workflow.

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.

5) Post ablation measurement of pits will also add significantly more time to the overall data workflow.

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.

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.

Section 2.4

Pb correction – good to see that no offset was observed, this reflects the observations and experience of myself and others but is good documentation of this fact.

Section 2.5 - WC-1 heterogeneity.

The authors state that "This finding demonstrates that WC-1 is not single-phased and heterogeneous in age."

I bring to the attention of the authors the following from Roberts et al. (2017): "A white alteration vein crossâĂŘcutting the mapped region is high in both Th and the transition metals." And "WCâĂŘ1 is not the perfect material because of its modest heterogeneity. . ."

Although this present study does not state that Roberts et al. (2017) claim a single-phased material, one might argue that is implied from their choice of phrasing.

For reference, Roberts et al. (2017) did not use the term 'single-phased', and openly quote the heterogeneity that they observe.

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.

I agree entirely that it is worth demonstrating this heterogeneity to others, since WC-1 is now a commonly used RM in the community. However, I would ask the authors to take care that their language better reflects the information presented in Roberts et al. (2017).

As the distributor of WC-1, I apologise for sending out an aliquot that had such a large altered region. I visually screen each piece, but after polishing down, some pieces will have worse regions than others. Altered regions should be avoided, as with any U-Pb or trace element reference material.

Line 241

"offset of 2-3%... of LA-ICP-MS results for ASH-15D compared to ID-TIMS results remains,. . ."

This sentence is written such that this offset should previously be described. But no description of this is provided. Therefore, what offset? And do the authors have a comment on what this means?

Summary

To reiterate the main points above, what needs changing:

1) The title. As far as I can see, this paper does not present new analytical and data

evaluation protocols. The paper provides data supporting the use of ablation condition matching, which is already the favoured method of most practitioners. Analytical protocols also follow those used by most labs already. The paper discusses a two-step strategy to normalise data with different aspect ratios, but then doesn't actually provide a detailed way of doing this, and goes on to say that not using this method would be better.

The paper does provide: A new potential RM, and data on matrix issues. This should be reflected in the title. e.g. "Evaluating the reliability of U-Pb LA-ICP-MS carbonate geochronology: matrix issues and a potential calcite reference material."

2) Present the data in a different light:

i.e. "we have documented the matrix issues in carbonate dating. . ."

i.e. "we document heterogeneity in the currently used WC-1, and present this information as a caution to analysts to make sure they understand that carbonates are heterogeneous materials, and care needs to be taken. . ."

i.e. "we present analytical data on a potential new calcite reference material. . ."

i.e. "we record a 2-2.5% long-term excess uncertainty, which may provide an ultimate limit on the uncertainty of carbonate U-Pb data. . ."

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