Geochronology Discuss.,
https://doi.org/10.5194/gchron-2020-17-AC1, 2020
© Author(s) 2020. This work is distributed under
the Creative Commons Attribution 4.0 License.

Interactive comment on "Expanding Limits of Laser-Ablation U-Pb Calcite Geochronology" *by* Andrew R. C. Kylander-Clark

Andrew R Kylander-Clark

kylander@geol.ucsb.edu

Received and published: 3 September 2020

Thank you for you review; your comments below are much appreciated, and I believe that, by addressing them, the manuscript is significantly improved. I have responded to each comment below and made changes to the manuscript accordingly. Original comments are shown and my responses follow follow each.

This paper presents laser ablation U-Pb calcite age data from a new MC-ICP-MS setup with multiple Daly detectors (including on the high mass side for U), and these data are compared with U measured on a Faraday cup on the same setup and by quad-ICP-MS on the same samples. Much of the paper discusses a theoretical model to explore the range of U, Pb, U/Pb ratios and samples ages that can be dated by the

new MC-ICPMS setup (with U on either the Faraday or Daly) and on a quadrupole. This is a very useful study, such that even if workers in the field do not have access new MC-ICP-MS setup, they will still benefit from the discussion on the U, Pb, U/Pb ratios and samples ages required to give data. It does need some changes though. The abstract barely mentions the theoretical modelling at all yet discussions based on it are a significant part of the paper, while some of the figures (figures 3 and 6 and to a lesser extent figure 1) require significantly more detailed and clearer figure captions to help the reader. More detail on the modelling would also be welcome, including making the source code available. The changes to the abstract are important, as the way it is currently written means the reader will not really know what is inside the paper. For example, while many papers have abstracts that are too similar to the conclusions, not one of the conclusions of this study (mainly based on the modelling) features in the abstract. The figure caption changes are definitely required for the reader to clearly follow the discussion on figures 3 and 6 (they will significantly improve its clarity and hence impact).

Response: The abstract has been modified to include more of the conclusions of the modelling. Content has been added to the Figures and their respective captions in order to improve their interpretations.

Minor comments Should the title be "Expanding the limits. . ." – I think it needs a definite article.

Response: "the" has been added

L38-40 "For typical LA-ICPMS analyses, a 193 nm excimer laser is employed in conjunction with either a single collector (SC-ICPMS), or multi-collector (MC-ICPMS) sector-field instrument to take advantage of the increased sensitivity over a quadrupole (Q-ICP-MS)." I think I will stick up for quads here. Several labs are now doing carbonate dating on the latest generation quads, so this statement is not really true. But it is also confusing, because the quad in this study is then referred to as an SC instrument

in lines 80-82. And the quad data presented in this paper are also pretty good – so I would reword L38-40."

Response: This is a fair point. We can also employ our quad for many of our calcite analyses. I clarified that SC can be a single collector on either a quad or sector field instrument and deleted the latter part of the sentence.

L52 you can also have covarying minor changes in U and Pb due to ICP flicker noise – simultaneous MC detection is beneficial for this too.

Response: A small line was added to incorporate this important point.

L60 “Because of its reduced sensitivity, however, this equates to a very small range of samples.” I think I know what you mean here, but is not very clear.

Response: This section was reworded for clarity.

L64 Not everyone will know too much about a Daly detector and maybe a small bit of extra info would be useful here. For example, in addition to its larger dynamic range, I thought they also exhibited more linear counting behaviour over this range?

Response: This should be true, but there are still similar corrections that need to be applied to both Daly and SEM detectors. Though they are different in design, they function in a similar fashion. The section was reworded to clarify this, and a short bit was added to point out their linearity.

L92 “Three calcite samples from the east coast of North America” is pretty vague. Veins? Speleothems? A line or two is all that is required.

Response: These are fault-related veins (Champlain Valley). This has been noted in the text.

L103-105 “The 238U/206Pb ratio was then corrected using a linear correction in Excel such that the primary calcite RM, WC-1, yielded 254 Ma (Roberts et al., 2017) on a Tera-Wasserburg (TW) diagram, anchored to a 207Pb/206Pb value of 0.85.” A bit

more detail needed here on the uncertainty propagation. For example is the initial uncertainty on the Pb ratio of WC-1 ($\pm$ 0.04) propagated through? For the Pb/Pb ratios, is the uncertainty on the NIST glass 207Pb/206Pb propagated through to the unknowns (see Drost et al., 2018, G3).

Response: These are good points and those doing geochronology should be aware of all the uncertainties and how they are treated. In the case of this study, a single value is used for the upper intercepts and NIST values because the idea is to compare the analytical uncertainties rather than use the actual ages of the samples to interpret a specific geologic event. This statement was added in the aforementioned section.

L115-121 I think it would be simpler to work in cps like in the rest of the paper (but put the mV equivalent in parentheses)

Response: Done.

L122-L129. Could be useful to cite a figure here – presumably figure 2 but also figure 1 could be brought back in (it doesn’t get much attention when first called out earlier on).

Response: Done. Figure 1 was cited with the first stated observation, and Figure 2 with the last stated observation.

L145-148 “Finally, though the Q-ICPMS shows similar gains in precision for low-U analyses, the lower sensitivity of the Q-ICPMS results in a minor window of U concentrations for which analyses have lower uncertainties than those run on the P3D.” I found latter part of this sentence hard to follow; could this minor window also be highlighted on Fig. 1?

Response: I reworded the sentence, referenced Figure 1b and also added a better explanation in the figure caption.

Section on “Theoretical uncertainty of Tera–Wasserburg data” L159 Is this a synthetic dataset?

Response: Yes. I added this to the sentence.

L165 Gerdes et al – what is this?

Response: Proper reference was added.

L172 – 174 “As depicted in Figure 3, older samples yield the greatest range of U/Pbc ratios that could yield an advantage of measurement by 238U on an ion counter, whereas the advantage of the Daly detector disappears at U/Pbc ratios greater than ca. 500 and 250 for samples that are 80 and 15 Ma, respectively.” But figure 3 only shows U/Pbc ratios up to 200. . ..

Response: This sentence was reworded to properly represent the figure. Though the figures only show a max U/Pbc of 200, the limitation value was calculated for 80 and 15 Ma. This is also stated.

Section on “Choosing Samples and Instruments” This section is too long not to have sub-headings. I think dsub-headings would really help focus it more.

Response: Sub-headings were added

L1901-191 “The distribution of U and Pb, and thus 238U/206Pb and 207Pb/206Pb, in calcite has not been a particular subject of study”. This is not strictly true - Roberts et al. (2020) (Figure 5 therein) do present U and total Pb data from a variety of samples – although admittedly none of their plots exclusively shows intra-sample variability – they are combined inter- and intra-sample variability (i.e. multiple spots from multiple samples). I also think Roberts et al. (2020) should be cited in this study.

Response: Agreed on all accounts – this study is particularly interested in the intra-sample variability, as that pertains to the expected uncertainties on a TW diagram. Roberts et al. has been cited.

L201-L204 – this needs reference to a figure.

Response: Figure 5d is now referenced

L209 “we present and discuss models. . .” How were these models made? Is the source code available?

Response: These models were created using Excel. They are fairly straightforward and can be made available on request. I have added a line to this effect.

L214-L224 again it would help if these samples could be put on one of the figure panels and the figure referred to in this section of text.

Response: Great suggestion. I added a star symbol to Figure 6(a,b,c) and referred to it in the text.

L229-L249 – again it would help again if these theoretical discussions could be labelled on the figure panels, with detailed reference to the figures from inside the main text. Several figure captions are really hard to wrap your head around – more detailed captioning and labelling is required.

Response: Added symbols for the examples given in text, and expanded the legend and caption in the figure. Âň Figure 1 – x-axis label unclear – move to below x-axis beside tick marks. What are the lines labelled 40%, 30% etc? Lines of equal RSD%? The U cps values for the large symbols show much higher sensitivities for the MC than the quad – nearly an order of magnitude(?), which appears to contradict the sensitivity differences quoted in lines 115-120.

Response: Axis label was moved. Lines labeled are percent uncertainties as opposed to absolute (y-axis). This has been clarified in the caption. The sensitivities are shown for the same spot size – the text in 115 describes analyses on the quad at 110 μm as opposed to 65 μm on the Nu. The figure shows $\sim$600 cps U for the quad and $\sim$3000 for the Nu (5 fold, rather than an order of magnitude). This is consistent with the text: 600 (cps for Q in Fig 1) *110ˆ2/65ˆ2 (Spot size difference) *2.7/1.8 (mV difference between Q and Nu in text) =$\sim$3000 (cps for Nu in Fig 1)

Figure 3. Label panels. I would rephrase along these lines to “Uncertainty ellipses on

each Tera–Wasserburg plot depict two end-member type of analyses, with the large ellipses representing the limit of detection for the all-Daly configuration, or any SCI-CPMS (limited by 207Pb counts), and the smaller red ellipses indicates the uncertainty at 30,000 cps 238U, the point at which the measurement of 238U on the Daly is no longer advantageous. The ellipses are coloured according to the 238U count rate, and depict the counting uncertainty for 10 s at this count rate for different U/Pbc ratios of 1, 2, 5, 10, 20, 50, 100, 200."

Response: The figure caption was changed and the panels are labeled and examples are given in each panel.

Figure 6 – panels are not labelled and the figure caption needs to explain what the coloured curves are. This figure caption needs the most work.

Response: Panels are now labeled. Examples from the text are inserted and labeled. The caption was expanded to better interpret the figure.

Interactive comment on Geochronology Discuss., https://doi.org/10.5194/gchron-2020-17, 2020.