

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

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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-ICP-MS 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.

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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).

David Chew

Minor comments

Should the title be “Expanding the limits. . .” – I think it needs a definite article.

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.

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.

L60 “Because of its reduced sensitivity, however, this equates to a very small range of

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samples.” I think I know what you mean here, but is not very clear.

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?

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.

L103-105 “The $^{238}\text{U}/^{206}\text{Pb}$ 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 $^{207}\text{Pb}/^{206}\text{Pb}$ 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 (± 0.04) propagated through? For the Pb/Pb ratios, is the uncertainty on the NIST glass $^{207}\text{Pb}/^{206}\text{Pb}$ propagated through to the unknowns (see Drost et al., 2018, G3).

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)

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).

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?

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

L165 Gerdes et al – what is this?

C3

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 ^{238}U 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. . . .

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.

L1901-191 “The distribution of U and Pb, and thus $^{238}\text{U}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$, 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.

L201-L204 – this needs reference to a figure.

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

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.

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.

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

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115-120.

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 SC-ICPMS (limited by ^{207}Pb counts), and the smaller red ellipses indicates the uncertainty at 30,000 cps ^{238}U , the point at which the measurement of ^{238}U on the Daly is no longer advantageous. The ellipses are coloured according to the ^{238}U 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.”

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.

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