Geochronology Discuss.,
https://doi.org/10.5194/gchron-2020-17-RC2, 2020

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

Randy Parrish (Referee)

randall.parrish@port.ac.uk

Received and published: 19 August 2020

Review of Kylander Clark: Expanding Calcite U-Pb dating

This is a paper detailing a methodology to do calcite U-Pb dating in which a very specialised instrument – the Nu Instruments P3D- is used which has multiple Daly ion counting detectors and an array of faraday cups. There are likely to be only a few of these instruments globally and so the main thrust of the paper is to show the specific advantages of this setup and to compare data with other, somewhat less sensitive instruments and detector arrays.

In a sense this paper is about doing 'traditional' calcite dating using a very specialised detector array. Aside from this demonstration of superior sensitivity, there are no par-

Printer-friendly version

Discussion paper

ticular advances within the paper that improve the way we do calcite dating, but the performance of this instrument is demonstrated to be reliable and is impressive for its ability to analyse samples with minimal U and Pb. It thus may go some distance to opening up the analysis of very low-U calcite samples at higher spatial resolution to address problems that are otherwise challenging.

Set up of the instrument.

Right away I see a flaw in the set up: there is no ion counter to measure the 232Th signal, only a faraday cup and with noise level of 8000cps, measuring 232Th is thus a write-off with no useful data likely to be collected in a majority of samples. Thus, it is unlikely to be quantified in order to measure radiogenic 208Pb as a contribution to the total 208Pb signal, which is the largest isotope comprising common Pb. I will come back to this.

At the end of this section the author makes a curious statement: Around line 110, The data from the unknowns are all a bit scattered for geological reasons, and were culled to yield single populations for ease of comparison. (Though beyond the scope of this manuscript, the Paleozoic samples are interpreted to have suffered partial Pb loss or new crystal growth in the Cretaceous–Tertiary, and the older Cretaceous sample likely (re)crystallized over an extended period.

When I read statements like this that suggest unknowns are all a bit scattered for geological reasons, it makes me wonder if this is just speculation, with some sort of analytical explanation for the scatter, at least in part, at play, and with the author(s) failing to examine the samples in depth to try to find out the explanation. It is so easy to suggest this sort of thing to explain messy data; in fact there are papers that invoke a wide range of unproven processes for scatter (U-loss, U-gain, Pb loss, variable common Pb composition; recrystallisation, etc.) all of which are just ad hoc explanations for scatter. The best approach, however, is to concentrate on such samples and try to really understand them with more measurements, particularly in their geological, hydrological, and textural context. There is little of this in this paper, largely because it is about methods, but this is an important point that all calcite dating people would do well to take more seriously.

Results

Results are on several reference materials and three different 'unknowns'. The WC-1 calcite is taken as the primary calcite reference material and all results are normalised using a secondary normalisation to the WC-1 calcite; this is standard practise and well documented by earlier papers. The three unknowns are not particularly young – 440 Ma, 120 Ma, and 80 Ma and the reference materials also treated as unknowns are Duff Brown (64 Ma) and Ash (3 Ma). Only WC-1 is very radiogenic; the others have a wide spread in U/Pb ratios. The approach used in all samples is to do regression of an array of spots on the assumption that all measured points are syngenetic and formed at the same time in each sample.

There is a comparison of the success rate and various other parameters that arise from the measurements of samples on the two instruments with the three set-ups. To no surprise, when U is very low, the faraday cup for its measurement performs relatively badly by comparison, but it still does work, to be fair. What is a little bit surprising is how the standard Q-ICP-MS performs so well in comparison to the ideal Daly set up of the Nu P3D, which is illustrated well in the plot of figure 1. What I notice about this figure is that, discounting the experiment with faraday 238U, there is almost complete overlap between the P3D setup with Daly 238U and the Q-ICP-MS, and to some extent a bit more scatter in the P3D data. The Daly is of course better at very high and very low count rates, due to its higher saturation count rate and its lower noise at low count rates, but the advantages of the P3D are not anywhere near as significant as I thought they might be.

The author composes synthetic sample calculations to illustrate the potential strengths and weaknesses of each instrument and setup and then in section 4.2 makes suggestions about which instrument and setup is best suited for unknowns. All of this is interesting, but largely a bit academic. The reality is that people who want to date calcite rarely have the luxury of having an initial session to measure their samples, establish a comprehensive picture of a sample's U and Pb concentrations, radiogenic to common proportions, and then have all of these set-ups available to them to then collect optimized data using the instrument/setup of choice. It will only rarely work that way. More often than not, samples have a geological significance and the challenge is to date as many of these samples as possible, as best as one can given the instrumentation available, and not to have to repeat the work unless necessary to answer ambiguities.

The other reality of all in situ dating, whether this be calcite LA-ICP-MS or accessory mineral SIMS or LA-ICP-MS, is that the Poisson 2SE precision on any ratio is never achievable, and usually with in situ dating, there is a +/-2% barrier that one cannot reduce. Calcite standards also have their own issues with absolute age such as WC-1 with its ~2% uncertainty in absolute age, and so to some extent the theoretical plots and analysis of this paper are not as applicable in practice as one would like.

The one aspect I cannot find well-described in this contribution is the manner in which the cross calibration of gains and linearity of the multiple Daly detectors have been determined. Has this been done detector by detector using experimental setups that establish ion counting gains and linearity independently? Or, is the use of the WC-1 with its range of count normalisation the method – in other words, if the standard and the other secondary standards give the right data by primary WC-1 normalistion, then all of these linearity and gain issues get accounted for by such a blanket normalisation 'fudge factor'? I suspect it's the latter and frankly it probably works ok, but the authors should be a lot more clear on this, since this is an obvious instrumental issue that is normally detailed in papers that collect multiple ion counter data.

Overall, this is a very careful piece of work with good analysis of the data. It offers some insight into the top level performance of the P3D instruments with its multiple

Daly detectors, and this helps all of us to understand what the benchmarks are as we evolve the techniques. I think the paper should be published largely as is (aside from the comment on ion counters above), because it is very well written and I can find no real issues with what has been done. However, below I comment on what has NOT been done that should be done on a subsequent comparative paper, ie., a followup study.

Additional comments:

Oftentimes in calcite dating, there is little justification in doing it for old samples, and almost all of the action is on younger calcites. This is because there will always be in situ dating uncertainties of +/-2% minimum, and so for a 440 Ma sample this means +/- 10 Ma at least, and many processes that are being studied cannot be resolved when uncertainties get so large. Therefore, the challenge is really to make the method work well for young samples. This study has largely skirted around younger samples but for a methodology to be highly relevant to most geologists, we need the resolution to be a few million years at most; hydrological processes are often fast and subject to disturbance and therefore, revealing tests of methods has to include doing work on very young samples with not so much low U but also very low radiogenic Pb contents. Because textures are complex and often in diagenetic settings, there is no reason to think that all secondary calcite formed at the same time, there is a strong need to be able to calculate single spot ages, like we do in accessory minerals. So far, few studies have done this.

So far the majority of calcite dating studies have ignored 208Pb and 232Th and instead used the T-W diagram for age calculations via regression. This has several problems:

1. Regressions assume all spots are the same age when this may not be the case; scatter is often glossed over

2. 207Pb that is radiogenic is the limiting factor on accuracy and precision. When a sample is young (say 20 Ma) and U is low (0.1 ppm), and when 207Pb background

noise is say 10cps, then the total radiogenic 207Pb might only be a factor of 1 or 2 above this noise, and no matter what setup is used, that will limit precision. Unless these low counts of 207Pb are accurate (and there can be issues when close to background), the ages may not be accurate either. The 207Pb common Pb correction is therefore critical when using the T-W plot, and it has real limitations.

3. This plot fails to use measurements of 232Th or 208Pb, which can be useful. Another way to do this in perhaps a more robust way is to use the 232Th and 208Pb in the plot with Y-axis being the 208Pbcommon/206Pbtotal and the X axis being 238U/206Pbtotal. Calcite rarely has high Th and so the subtraction of 208Pbradiogenic is often trivial, allowing the common Pb correction to be done independently of a radiogenic isotope like 207Pb.

When the author stated early on in the manuscript that data are a bit scattered, I think it is possible if not probable that there may be issues in the measurement of the small 207Pb radiogenic component that could be mitigated if one does not rely upon measurement of 207Pb and instead takes advantage of the 208Pb measurement (virtually all common) and 232Th (usually very low). I discuss this in Parrish et al. (2017) and showed that often this approach works better.

Secondly, readers of this sort of paper should always remember that the field of ICP-MS and particular LA-ICP-MS has seen many orders of magnitude improvement in sensitivity by the use of multiple quads, collision cells, and the like. It is never a good idea to take a standard ICP-MS such as that used in the measurements of this paper, as truly representative of the sensitivity of Q-ICP-MS instruments which can achieve sensitivities nearly as good as MC-ICP-MS in like-for-like experiments. This is just a caution.

I would also love to see the author undertake some testing of individual spot ages using various methods, spot sizes, and so forth to evaluate the power of the P3D instrument to really outcompete Q-ICP-MS in challenging texturally complex samples that require smaller spot sizes to resolve texturally complex calcite/dolomite growth components. This is where I think the P3D might really have some clear blue water ahead of the other instruments. The application of instrument comparisons on older samples using just the isochron technique is, I think, NOT where the most interesting comparisons of methods of calcite dating are likely to be done. I hope something along these lines might be next project for the author.

R Parrish, 19 August 2020

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