Geochronology Discuss., referee comment RC2
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Comment on gchron-2021-46

Nick Roberts (Referee)

Referee comment on "In situ Lu–Hf geochronology of calcite" by Alexander Simpson et al., Geochronology Discuss., https://doi.org/10.5194/gchron-2021-46-RC2, 2022

Review of GChron-2021-46

Simpson et al.

Summary

This paper presents results of Lu-Hf dating of calcite using laser ablation ICP-MS via a 'triple-quad' or 'tandem MS/MS instrument. The paper follows on from a previous paper by the same group that presented the method for dating of garnet and apatite.

The paper is not really a 'method' paper, in that the method description is sparse, and mostly just refers to the previous paper. Also, few details on the nuances of this method – what works and what

does not for example, are included.

The method is novel and exciting, and therefore this data should be published to spark interest from other groups, and to get the community talking about reference materials and best practices.

Overall, I feel the detail is too scant, and relies heavily on the previous paper from the group. However, I do not feel the reader should have to refer back to this paper for everything, and for calcite specific issues the detail should be revaluated here.

Comments

The data are normalised to MKED calcite – but it is not made clear what is used. The titanite age is used and the calcite is assumed to be the same age?

Although the same conditions may be used as in Simpson et al. 2021, it is best practise to

publish an analytical protocol metadata table for each paper.

As stated in Simpson et al. 2021, common Hf corrections may not be applicable to all samples. This paper does not mention any caveats with the approach, but should.

From the other reviewer "It is better to celebrate the data by letting them speak for themselves, rather than reiterating how good they are after every paragraph of the discussion." I full accord with this!

I feel there is little value in going for the minimum number of figures in a method paper.

Uncertainty propagation

In situ U-Pb geochronology is now in its third decade, and yet uncertainty propagation is still an issue, and not consistent across groups. However, that is not an excuse for ignoring the issues with other chronometers, in fact, it means we can take the overall approach used in U-Pb and apply it elsewhere.

In summary, any 'final' quoted age should include propagation of systematic uncertainties, and for in situ geochronology, these will always incorporate 1) the decay constant uncertainty of the system in question, 2) any uncertainty on a propagated constant such as common lead or common Hf, 3) any uncertainty where a proxy ratio is used for another (e.g. on the natural 177/178 ratio), 4) the long-term reproducibility of the validation materials. Additionally, the uncertainty of the primary reference material measurements

are propagated onto the individual datapoints themselves.

Although long-term reproducibility will be impossible to determine at this stage, other aspects of the uncertainty propagation can be determined.

This paper does not describe any aspect of what has been propagated and what hasn't. Although it can stated that full propagation at this stage may be premature, because of some unknowns, there should be some statement about what the quoted uncertainties include.

Uncertainties in the abstract are quoted as between 1.4 and 0.5%.

I note that Nebel et al 2009 has 0.3% for the Lu-Hf ratio in NIST 610, which is significant, and 0.003 for the Hf-Hf ratio, which is obviously insignificant (but can still be included where appropriate).

Figures

The sample images are too small to be useful, and more detailed images that are relevant to the paragenesis of the mineral assemblage can be placed in the supp files.

I would prefer to see isochron plots as well.

Data-Tables

There are two sets for P01 and it is not clear how they relate to the single figure in the paper.

Same goes for ME1 – different sessions?

LC1 – there is an outlier removed and this isn’t mentioned.

Line by line:

Line 18 – “Suspendisse” Not sure why this is written here?!

Line 19 – I’m not sure this is best way of describing the abundant formation locations of calcite – I would certainly add that it is a common diagenetic phase.

Line 30 – This could be reference with some of the older papers – Russell and Whitehouse?

Line 32 – radioisotopic is the preferred term these days.

Line 32 – I would add an older reference for Sm-Nd too, there are several.

Line 34 – other papers for REE incorporation in calcite could be added – certainly more older seminal works.

Line 36 – I would argue it better to say “potentially less susceptible”. This statement is rather conjectural, and mobility is strongly dependant on the redix conditions, which will influence Lu-Hf and U-Pb differently.

Line 37 – ppt in fact!

Line 40 - “mixed age” is probably a bit confusing. What you mean is an average age of what could be mixed ages within the sample.

Line 42 – do we need all 5 papers cited given that they are all garnet and from the same lab?

Line 46 – “demonstrate the power… for complexly deformed and hydrothermally-altered systems”

Line 47 – I think a little overstated “if not impossible” – what are traditional methods these days? Most people will attempt multi-mineral and multi-isotopic work, such as common-lead bearing minerals.

Line 58 – I think it prudent to mention which mineral and which method here, i.e. zircon by SIMS. Since some readers know that a published age is not necessarily as simple as it seems. In this case, an age uncertainty rather small (0.1%) compared to the long-term accuracy and precision of SIMS 7-6 ages.

Line 74 – grammar

Line 77 – "good constraints on expected mineralisation ages" Although the age span covers 50 Myrs still.

Line 138 – cannot see enough detail in the figure of this sample – see comment above.

Line 142-144 – stick with one timeframe (and note that this is merely the last and main phase of the orogeny – which could be stated).

Line 179 – what is negligible? A number in some form would be useful, rather than referring back to the previous paper all the time.

Line 180 - 175Lu as a proxy for 176Lu – uncertainty derived on that?

Line 181 – 178Hf as a proxy for 177Hf – uncertainty derived on that?

Line 182 – state the isotopic abundances here.

Line 183 – dwell times? Add table

Line 183 – show a time-resolved scan figure with inclusions?

Line 187 – "NIST SRM 610 glass was used as the primary reference material" reference for values here.

Line 188 – different spot size for NIST – need to show the accuracy of this, and not just refer to Simpson et al. 2021.

Line 189 – this was shown for apatite and garnet. I would strongly argue that this needs to be demonstrated here for calcite, even if the point is deemed pedantic.

Line 189 - one should also state that there is “no measurable downhole fractionation” (i.e. using this instrumentation), that is not the same as having no downhole fractionation.

Line 201-206 – This will of course vary from instrument set-up to instrument set-up, but it is still nice to see this observation made.

Line 208 – grammar

Line 214 – what were these detection limits – can you quantify?

Line 214-218 – so common Hf corrected on a cycle by cycle basis – it would be useful to see this compared with a correction upon the entire ablation, and the uncertainty contribution from this correction.

Line 227 – “Further details are outlined in supplementary file 3” I don’t see any details. Just some plots and some data using this method.

Line 238 – I do not see any info on what the assumed common Hf ratio is, nor what it is determined by.

Line 272 - “The slight difference between the calcite Lu–Hf age 273 (894 ± 12 Ma) and apatite Pb-Pb age (913 ± 7 Ma)” I suspect this is due only to under-estimated uncertainty budgets.

Line 292 – 0.5-1.7% - different values from the abstract.

Line 301 - in some hydrothermal settings yes, but many settings the calcite is always less than 100 microns.

Line 306 – This type of statement is seen commonly, but is nearly always due to low precision of in situ methods masking any heterogeneity. There is no need to 'sell' the method. Just write the facts.

Line 305 – "well constrained ages" is rather subjective – given the very large size of the individual datapoint uncertainties of this study.

Line 311 – although the comparison of thermal diffusion is relevant – it is fluid-mobility that is much more important for calcite as a chronometer – and I don't know what data there is on Lu and Hf.