Reviewer 1 comments and replies:

I find this to be a strikingly innovative work that shows the power of reaction cell technology for separating isobars and documents the application of Lu/Hf dating of Precambrian calcite from a variety of igneous, metamorphic and hydrothermal settings using LA-ICPMS. The results are of high quality and should be of broad interest.

Dear Don Davis. Thank you very much for your helpful comments and interest in our research.

The presentation has a few problems, particularly regarding the use of Supplementary Data files, that are outlined below. Aside from this, my comments are mostly minor and are given below as well as annotations to the manuscript file.

Lines 9 & 166

Strictly speaking, the Agilent 7900 is a tandem mass spectrometer but historically this term referred to sector magnetic instruments, which caused me some confusion when I first read the abstract. Why not refer to it the same way the company does: a triple quadrupole?

Our understanding is that the term 'triple quadrupole' is brand specific (to Agilent) and the geoscience community is moving toward a more generic term: MS/MS.

We have carefully looked further into this comment and it appears that the correct term is tandem quadrupole mass spectrometry, rather than tandem mass spectrometry. We will correct this in the revised manuscript. We will also add the term 'triple quadrupole' when MS/MS it is first mentioned, to make it clear that this is another name for the type of mass spectrometer we have used.

References to Supplementary files and figures in Lines 161, 169, 227, 239, 494.

These appear to be incomplete and confusing. I could not find any supplementary text files. There are no captions for the supplementary figures. Supplementary File 1 in lines 239 and 494 presumably refers to Supplementary Table 1.

Thanks for pointing this out. We will thoroughly go over these lines and update the figure captions in supplementary file 1.

Line 204

The main problem that I have noticed with ablating large amounts of calcite is the prevalence of signal spikes due to dislodging chunks of incompletely ablated sample from the walls of the He tubing, the mixing chamber and the plasma torch. Forcing compressed N2 (not compressed air from the lab outlet as it tends to contain oil) back through the ablation chamber tube at its outlet with the sample chamber removed, replacing the external tygon tubing and ultrasonicating the mixing chamber and plasma torch in alcohol reduces this problem. We haven't found a big problem with the cones, although a thick coating might become charged, reducing transmission, so they should be periodically cleaned.

Thanks for the comment. We used a similar procedure for cleaning our tubing and will further clarify that this is important to do after ablating large quantities of carbonate.

The large laser beam diameters we have used tends to deposit coatings on the cones and to mitigate this, it`s important to keep calcite Lu-Hf runs rather short (and carefully clean the cones afterwards).

We plan to expand this section (including reference to cleaning procedures, such as the one you mentioned) in the revised manuscript.

Figure 3

Instead of presenting ordered age error bars as now shown, more information would be given by plotting the analyses using inverse (177Hf/176Hf vs 176Lu/176Hf) diagrams with 2 sigma error ellipses along with the best fit line forced through the assumed initial (176Hf/177Hf)c value. Although it is a bit more work, the isochron could be marked off with % values of radiogenic 176Hf. 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.

Yes, thank you for this comment, this would be a good alternative way of presenting the data (and produces effectively the same result as the Hf corrected data.)

It may be somewhat redundant to include both a common-Hf corrected weighted average plot and (inverse) isochron plot, given both are effectively 'anchored' to the same value.

However, we will give this some thoughts and either add the inverse isochrons in the supplementary materials or as part of the results figure in the manuscript.

Alex Simpson and co-authors

Reviewer 2 comments and replies:

The following changes have been made to this version relative to the one posted as a reply to the reviewer comments:

1. A new figure demonstrating that down-hole fractionation does not occur in calcite analysed with a laser spot size of 257 microns has <u>not</u> been made, as we realised that fig. 2 already shows this.
2. A figure demonstrating that NIST610 analysed at a laser spot size of 43 microns has not been made as this is already demonstrated in Simpson et al., 2021a, and no down-hole correction is applied to the data
3. Different sessions of sample P01 have not been colour coded on the figure, but the text has been modified to explain that this sample (and ME1) were analysed over multiple sessions.

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.

See response to detailed comments below

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?

Details of the MKED calcite is presented in supplementary file 3, which was unfortunately missing from the submission.

This supplementary file was probably not uploaded correctly as Gchron prefers this kind of information to be included as an appendix. As such we have added the information that was missing as appendices. Please see further comments for specific information about the added appendices.

Added to line 248 of main text: '…were corrected to MKED calcite. Although the age of MKED calcite is currently not independently constrained, calcite is interpreted from textural evidence to have formed with the MKED titanite reference material, and therefore the titanite TIMS U-Pb age was used (1517.32 ± 0.32 Ma; Spandler et al., 2016). Further details are outlined in appendix A'

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.

This table was included in the original supplementary file 3.

It is now included in the appendix (line 639).

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.

We have expanded this to acknowledge that corrections should not be used, or should be used with caution when applied to data with a high common Hf.

However, the data presented here is not sufficient to apply an exact cut-off, as such, we have simply stated that if common Hf is higher than the data presented here (particularly if significantly higher), corrections should be used with caution.

Added lines 237 "The uncertainty on the initial ^{176}Hf/^{178}Hf ratio used for the common Hf corrections has been propagated to the final ages. However, as most analyses have <1% common Hf (Table 1), any inaccuracy related to the initial ^{176}Hf/^{178}Hf ratio is negligible compared to the total uncertainty estimates given Hf isotopes do not vary significantly with time (Fisher and Vervoort, 2018; Vervoort, 2014). Such corrections, however, should be used with caution for samples with higher common Hf, although the dataset presented in this study is not sufficient to determine what an appropriate cutoff should be."

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!

Deleted line 300 'These distinct ages obtained for different mineral parageneses from the same IOCG deposit demonstrates the power of in-situ Lu–Hf dating to not only provide direct ages of mineralisation, but also to interrogate multiple alteration events within a single deposit.'

Modified line 335 to 'In summary, we demonstrate that *in-situ* Lu–Hf geochronology can produce geologically meaningful ages for calcite from a variety of mineralisation styles (e.g. IOCG, carbonatite, and skarn alteration) as well as greenschist-facies metamorphism'

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

We will add both ways of plotting the data to the next version!

Modified figure 3 to include both inverse isochrons and weighted average ages.

One thing to mention is that analyses with 178Hf below detection cannot be plotted on isochron plots but these data are potentially the most precise.

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.

Yes, the session to session plots for MKED and Mt Elliott 1 show insignificant variation between sessions (this would have been made more clear in the missing supplementary data), but as you say, we need more data!

We have added line 272 to the paragraph on uncertainty propagation: 'Uncertainty relating to long term reproducibility of the MKED secondary standard has not been propagated, as the standard data for all 4 sessions does not show excess scatter (MSWD =1). More data, however, is required to fully constrain this.

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.

We have added a paragraph to the main text on uncertainty propagation, detailing the steps we have taken (and added based on the reviewer's comments).

Lines 259: 'Correct handling of uncertainties in geochronology is important in order to draw accurate conclusions about the resulting ages. As per the recommendations for LA-ICP-MS U-Pb uncertainty propagation in Horstwood et al. (2016), uncertainties are categorised as random, in which case they are propagated to individual analyses, or systematic, in which case they are propagated to the final calculated age. As such, the uncertainties associated with the measurement of the primary standard (NIST SRM 610) have been propagated to the uncertainties of individual analyses. The following systematic uncertainties have been propagated to the final ages; measurement uncertainty on the secondary standard (MKED C); uncertainty on the titanite U-Pb age used as the reference age for MKED C; uncertainties associated with the ^{176}Lu decay constant, and; the reference ^{176}Hf/^{177}Hf ratios for NIST 610 SRM. Although for completeness uncertainty relating to potential differences in ^{175}Lu/^{176}Lu and ^{177}Hf/^{178}Hf between NIST 610 SRM and samples should also be propagated (i.e. natural variation in these ratios), however there currently is no data on this. These uncertainties are likely to be negligible relative to the overall uncertainty estimates for the analyses. The uncertainty associated with the reference ^{176}Lu/^{177}Hf, ^{176}Lu/^{176}Hf, and ^{176}Hf/^{176}Lu ratios of NIST 610 SRM are not propagated, as the correction factor associated with NIST 610 SRM is cancelled during the correction to MKED calcite (as the NIST 610 SRM correction factor is applied equally to MKED calcite and the unknowns samples, and thus cancels out). Uncertainty relating to long term reproducibility of the standards has not been propagated, as the standard data for all sessions does not show excess scatter. More data, however, is required to fully constrain this.'

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).

Technically, I think you could make a case that the uncertainty on the NIST $^{176}Lu/^{177}Hf$ and $^{176}Lu/^{176}Hf$ from Nebel et al., 2009 should not be propagated, as the correction to NIST is cancelled by the subsequent correction to MKED calcite. This is because the NIST correction is applied equally to both unknowns *and* MKED calcite.

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.

We have added larger and more detailed images of the appendices/supplementary figures. These are now separate figures with separate captions

Mostly these are larger/expanded versions of the current figures that make mineralogy/textural relationships easier to see.

We have also changed the format of the current figure to fit a full A4 page, hopefully this makes the sample images much easier to see.

I would prefer to see isochron plots as well.

Modified figure 3 to show both inverse isochrons and weighted average Hf corrected ages.

Data-Tables

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

These are from two different analytical sessions. We have acknowledged this in the text:

Line 283: 'Due to the large number of inclusions, P01 was analysed over two sessions'

Same goes for ME1 – different sessions?

Yes, I think this is explained in more detail in the missing supplementary file! but we have added this to the main text to clarify (for all samples that were run over more than one session)

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

Data points with inclusions/zonation are removed from a few samples, and we have modified the main text to acknowledge this.

Added lines 280 'For analyses with inclusions, the signals have been cropped to remove inclusions or, in the case of more significant signal disturbances, excluded from age

calculations. Inclusions were detected in the following samples: MKED calcite (6), LC1 (1), P01 (19) and FF014 (6). Excluded data points are included in supplementary file 1.'

Line by line:

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

We are not sure either! This has been removed

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.

Modified line 18 to 'Calcite ($CaCO_3$) is the main mineral phase of most carbonate sedimentary rocks and their metamorphic equivalents, is a common diagenetic phase and is a major component of carbonatites.'

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

Added reference to Russell and Whitehouse to line 30

Line 32 – radioisotopic is the preferred term these days.

Changed radiometric to radioisotopic in line 32

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

We have added the following references: Barker et al., 2009, Nie et al., 1999, and Peng et al., 2003.

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

Added the following references: Zhong and Mucci, 1995, Terakado and Masuda, 1988, and Elzinga et al., 2002.

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.

Added 'potentially less susceptible' to line 38

Line 37 – ppt in fact!

Changed to ppm - ppt

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.

Changed line 42 to make it more clear '… produce a meaningless average age derived from mixing of age domains

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

Yes, perhaps this is too many self-citations!

We have changed this to recognise the garnet application papers published at the time of writing (Ribiero et al and Tamblyn et al) and the apatite paper that is also published (Glorie et al).

Changed line 43 to 'The recent development of *in-situ* Lu–Hf geochronology of individual minerals by LA-ICP-MS/MS allows for rapid acquisition of spatially resolved data, and has been demonstrated for garnet (Ribeiro et al., 2021; Tamblyn et al., 2021) and apatite (Glorie et al., 2021)'

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.

Lines 46 and 47 have been rewritten as follows:

(line 47) to 'We demonstrate that *in-situ* calcite Lu–Hf geochronology can produce meaningful ages for complexly deformed and hydrothermally-altered systems, such as mineral deposits, as well as for carbonatites and calcite-bearing metamorphic rocks.'

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.

Changed line 59 to include reference to the method used (added 'baddeleyite SIMS U-Pb')

Line 74 – grammar

Modified line 75 to 'Hydrothermal calcite is common across the Mount Isa region, including in the Mary Kathleen Domain (Oliver et al., 1993) and in many of the IOCG deposit of the Cloncurry District'

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

We have modified the text to better describe why this is a useful area to test the presented technique:

Changed line 78 to 'The Mt Isa Domain has both regional and deposit level age constraints, making it a good area to demonstrate the technique.'

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

Modified this figure (1) to make it bigger.

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).

Most modern references seem to give 1080-980 Ma as the Grenvillian orogeny (e.g. the 2021 edition of the Encyclopaedia of geology) – it seems that early phases may be classified as separate orogenies (?).

We have removed reference to both time frames and stuck with 1080-980 Ma (note that this is slightly different to the original 1080-985 Ma.)

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

Modified line 179: 'This method minimizes the equivalent Lu and Yb reaction products (~0.03% for Lu, and below detection for Yb), such that the isobaric interferences on 176Hf are negligible (Simpson et al., 2021a).'

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.

The above three comments are addressed together:

The line we have used here was a bit misleading. We are actually normalising our Lu/Hf directly to NIST. So for instance, a correction factor is calculated from the (NIST measured) ^{176}Hf(+82)/^{175}Lu divided by the ^{176}Hf/^{176}Lu ratio calculated from the published ratios in Nebel et al., 2009. This correction factor is then applied to the unknown ^{176}Hf(+82)/^{175}Lu ratios. This method should be mathematically correct assuming that the ^{176}Lu/^{175}Lu ratios are identical between NIST and the unknowns. The same approach is applied to ratios that require ^{177}Hf to be calculated from measured ^{178}Hf.

It might be appropriate to propagate an uncertainty relating to any potential variations in ^{175}Lu/^{175}Lu or ^{177}Hf/^{178}Hf ratios (to account for potential differences between NIST 610 and the unknowns), but this is difficult to constrain, and likely extremely small compared to the rest of the uncertainty (would not change the uncertainty within significant figures).

There appears to be no data on natural variation in these isotopes either (which would be a better proxy for uncertainty, I think). Measurement uncertainties are generally so precise that they would make essentially no difference to the calculated uncertainties. As such we have acknowledged this in the text, but not propagated any uncertainty.

We have also modified the text to better explain how the ratios are calculated (and added a more detailed explanation to the appendices).

Modified lines 181: 'In order to calculate Lu/Hf ratios, ^{176}Hf (+82) was measured directly, ^{175}Lu was measured as a proxy for ^{176}Lu, and ^{178}Hf (+82) measured as a proxy for ^{177}Hf (Simpson et al., 2021a). ^{176}Hf/^{176}Lu, ^{176}Lu/^{177}Hf, and ^{176}Hf/^{177}Hf ratios were calculated as part of the normalization to NIST610, as opposed to separately converting measured ^{175}Lu and ^{178}Hf into ^{176}Lu and ^{178}Hf. In more detail, if we assume that the ^{176}Lu/^{175}Lu ratio (or ^{177}HF/^{178}Hf ratio) is identical between NIST SRM 610 and all analysed samples, a correction factor calculated from the % difference between the ^{175}Lu/^{178}Hf ratio measured in NIST SRM 610 and the published ^{176}Lu/^{177}Hf will convert the ^{175}Lu/^{178}Hf ratios into ^{176}Lu/^{177}Hf ratios, as well as correct for mass bias and matrix independent fractionation.

Line 183 – dwell times? Add table

This was included in the meta data table in the missing supplementary file, which is now in the appendix

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

The presence (and removal) of inclusions in laser ablation data is not new to the method we are presenting here. No changes made.

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

There is a reference to the Nebel et al., 2009 paper further in the methods section, but we agree that it is also appropriate here (and have added the exact ratios we have used)

Modified line 194 to 'NIST SRM 610 glass (176Lu/177Hf: 0.1379 ± 0.005, 176Hf/177Hf: 0.282122 ± 0.000009; Nebel et al., 2009) was used as the primary reference material and was analyzed using a spot size of 43 µm.'

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

We have decided not to make any changes, as 1) no downhole correction was applied to the data, 2) the original Simpson et al., 2021 paper demonstrates that NIST610 does not undergo down-hole fractionation at a spot size diameter of 43 microns and 3) any offset induced by issues with the correction to NIST610 are subsequently corrected by our matrix matched secondary standard correction (to MKED C).

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.

Figure 2 already shows this (albeit for different reasons) we have modified the text and figure caption to acknowledge this:

Line 196: 'Consistent with observations in Simpson et al. (2021a), Lu and Hf showed no measureable down-hole fractionation in the analysed carbonates (fig. 2), as such, no down-hole correction was applied to the data.'

Figure caption; line 591 - 'Time resolved signals for $^{175}Lu/^{(176)}Hf$ (+82), ^{43}Ca, ^{175}Lu, and $^{(176))}Hf$ (+82) demonstrating the effects of plasma loading on the signal intensities (i.e. dip in signal intensities at ~10-15s ablation), but not for the $^{176}Hf/^{175}Lu$ ratio, which remains constant down-hole.'

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.

Changed line 197 to 'Consistent with observations in Simpson et al. (2021a), Lu and Hf showed no measureable down-hole fractionation in the analysed carbonates'

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.

We have expanded this section to acknowledge that there may be differences between instruments, as well as discuss other potential issues relating to the amount of ablated material.

Added line 214 'In addition to this, the accumulated material was sometimes mobilized in later analyses, potentially contaminating data. This was observed by increases in Al during the start of ablation that decayed down to background levels. Importantly, similar Al spikes were not observed during background measurement, indicating contamination due to material remobilized during ablation is likely, hence why the additional 20 seconds of washout did not fix this. This contamination did not generally produce a measurable effect on calculated Lu/Hf ratios. However, we stress that this contamination is important to monitor as Hf concentrations are sometimes in the ppt level. As such we recommend close monitoring of signals, particularly Al concentrations, and the removal of 1-3 seconds of each analysis after signal stabilisation if necessary. '

Line 208 – grammar

This line has been removed and the following line has been modified (line 222): 'For both LA-ICP-MS and LA-ICP-MS/MS analysis, a stoichiometric Ca concentration of 40.04 wt.% for calcite was used for internal normalization of trace element concentrations'

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

The LADR data reduction software outputs calculate detection limits. We have added reference to this to the text.

Modified line 229: 'Where ^{178}Hf was measured above detection limits (~2 ppt for ^{178}Hf), common Hf corrections were applied to the data after background subtractions, but prior to normalization to the standard.'

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.

The cycle by cycle uncertainties are considered more accurate as the common Hf can vary during an analysis.

The advantage of the cycle by cycle approach is that the uncertainty can be directly calculated from the resulting common Hf corrected 176Hf, rather than calculating using an estimate based on the standard deviation of the 178Hf and 176Hf measurements.

This is a similar concept to why it is common practise to calculate the average ratio rather than the ratio of averages in isotope ratio analysis.

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.

This should now be in the appendix A

Changed line 251 to '… further details are outlined in appendix A'

Added appendix A: 'A sample of orange-pink calcite associated with the MKED1 titanite U-Pb standard (1517.32 ± 0.32 Ma, U-Pb TIMS; Spandler et al., 2016) was analysed as a matrix matched secondary standard in order to correct unknown samples for matrix related analytical offsets, such as laser induced elemental fractionation and plasma loading effects. The calcite was sampled from the same drill core from which the titanite standard was taken (full details can be found in Spandler et al., 2016). The sample consists of massive calcite-titanite veins with the calcite interpreted to be texturally cogenetic with large (~8cm) euhedral titanite crystals. The titanite is interpreted to have grown in the same fluid as the calcite, but just prior to calcite crystallization. The average age across all 4 analytic sessions is 1560 ± 10 Ma (supplementary fig. 3), indicating that matrix fractionation during laser ablation produces ages that are systematically approximately 3% too old'

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

We have modified the text to clarify the ratios used, as well as the uncertainty associated with this value.

Added lines 235 'These corrections were applied using an assumed initial ^{176}Hf/^{178}Hf ratio of 0.192 ± 0.004, which is equivalent to a ^{176}Hf/^{177}Hf ratio of 0.2816 ± 0.006. This value is based on the Hf evolution of the crust (Spencer et al., 2020; Vervoort, 2014; Vervoort and Patchett, 1996), with uncertainty that comfortably covers likely natural variation.'

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.

This may be the case, however, it would require a fairly significant under estimate of the uncertainties for these to be likely to be the same event. We have mainly included this line as multiple U-Pb ages have been produced from single Otter Lake apatite crystals, so we feel it is more appropriate to be cautious about whether these ages are the same (or not).

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

We have recalculated the total uncertainty for each sample and modified the figures and text to reflect this.

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

We have modified the text to acknowledge this and better explain what we mean.

Added line 345: 'Additionally, particularly in hydrothermal settings, calcite often forms large, mm to cm scale crystals, reducing the need for small ablation volumes. While individual calcite crystals in other settings can sometimes be < 260 µm, the total amount of calcite is often large enough that aggregates of pure (or close to pure) calcite can be ablated. Caution should be used with such analysis however, as this may effect laser induced fractionation, individual crystals may be of different ages, and there may be micro inclusions of other Lu or Hf containing minerals.'

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.

Is this the wrong line number? Are you referring to the line about scattered isochrons in solution work? (Line 306 talks about spatial resolution).

Anyway, we have deleted this bit and rewritten the start of this paragraph (note that this covers the following comment as well (line 347): 'The Previous dissolution-based Lu–Hf geochronology has produced scattered isochrons, indicative of isotopic disturbances (Maas et al., 2020). While individual calcite crystals in other settings are often sub 260 µm in size, the total amount of calcite is often large enough that aggregates of pure (or close to pure) calcite can be ablated. Caution should be used with such analysis however, as this may effect laser induced fractionation, individual crystals may be of different ages, and there may be micro inclusions of other minerals.'

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

See above comment

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.

Yes, it is also worth acknowledging that re-crystallisation is likely to reset the Lu-Hf system too.

Added line 361 'Nevertheless, it should be acknowledged that the effects of fluid alteration and re-crystallisation of calcite on Lu-Hf ages are difficult to predict'