

[Point-by-point reply to the reviewers' comments \(our responses in red below\).](#)

## Comment on gchron-2022-21

Graham Edwards (Referee)

Referee comment on "*In situ* U-Pb dating of 4 billion year old carbonates in martian meteorite Allan Hills 84001" by Romain Tartèse and Ian C. Lyon, *Geochronology Discuss.*, <https://doi.org/10.5194/gchron-2022-21-RC1>, 2022

### Overview

In this manuscript, the authors describe an analytical approach to measuring U-Pb isotopes *in situ* in carbonate minerals of the Martian meteorite ALH 84001. They report U-Pb and Pb-Pb dates that overlap with prior bulk isochron dates of the Rb-Sr and Pb-Pb systems. Based on this intra- and inter-system concordance, they concur with prior studies that ALH 84001 has experienced minimal disturbance since its primary carbonate system "closure." In addition, this study provides a compelling proof-of-concept discussion on the precision capable with U-Pb dating by SIMS in multi-Ga carbonates, and the authors thoughtfully comment on where analytical and standardization improvements are needed for further improvement of these approaches.

The methods and interpretations in this study are overall rigorous and sound. My major criticism of this manuscript is that the authors offer only limited interpretation of the geologic (or areologic, if preferred) implications of the uneventful history recorded by ALH 84001 carbonates. In particular, I believe that this manuscript would benefit from expanded discussion on the implications of low common Pb content in the carbonate-forming fluids and the implications of multi-system concordance for the geologic and impact/post-impact history of ALH 84001. While not strictly necessary, I think the manuscript falls short of its potential without broader discussion/interpretation of the results.

I recommend this manuscript for publication in *Geochronology*, so long as the following comments are sufficiently addressed.

Respectfully,  
Graham Edwards

**Tartese & Lyon: We thank Graham Edwards for their constructive and supportive review of our study. We explain below how we have addressed all their suggestions.**

### Specific Comments

- Did different carbonate lithologies/mineralogies manifest different U-Pb systematics? From a cursory look at Table S3, it appears there was not a difference, but potential differences in the two mineralogies should be examined. If indeed the systems show similar systematics, that adds further support to the authors' conclusions of the undisturbed history of ALH 84001 carbonates.

**Tartese & Lyon: The Mg-rich carbonate analyses yield a concordia date of  $3890 \pm 72$  Ma (2 sigma, MSWD conc. + equ. = 1.5, n = 8), while the Ca-rich carbonate analyses yield a concordia date of  $3995 \pm 69$  Ma (2 sigma, MSWD conc. + equ. = 2.4, n = 6). The U-Pb dates**

for these two carbonate compositions are, therefore, indistinguishable when uncertainties are considered. We have added this short discussion in the revised ms.

- Along similar lines, there does not appear to be a difference between the U-Pb and Pb-Pb dates of the two different mineralogies (Table S3), implying a common origin. I recommend the authors comment on how this informs the mechanisms of carbonate formation in ALH 84001.

Tartese & Lyon: As mentioned just above, the U-Pb and Pb/Pb dates for these two carbonate compositions are indistinguishable when uncertainties are considered. These uncertainties are fairly large though, so it would be quite speculative to infer further on the formation mechanisms for the variable carbonate compositions, and notably whether they represent a continuum of formation with changing fluid composition or several discrete events implying different fluids.

- There is some linear spread in the U-Pb data of WC-1 in Fig. S1. Is this accounted for in the use of WC-1 as a standard for U-Pb fractionation? If so, how? If not, the authors must justify why a correction is not necessary and/or how any corresponding uncertainty is propagated. This variation does not appear to be within the 2.5% uncertainty used to account for uncertainty in the age, though I may be mistaken.

Tartese & Lyon: There is indeed some linear spread in our WC-1 analyses, which is consistent with *ca.* 7-15% common Pb component in the analyses volumes. This is known (e.g., Roberts et al., 2017), and does not really affect its use as a primary standard. In fact, it helps construct an isochron, anchored at the WC-1 common  $^{207}\text{Pb}/^{206}\text{Pb}$  ratio of 0.85, which gives us a lower intercept date. This is this difference between the ‘measured’ intercept date and the WC-1 ‘known’ formation age of  $254.4 \pm 6.4$  Ma that is used to correct for U/Pb instrumental fractionation, a common practice in carbonate U-Pb dating by LA-ICP-MS.

- While the authors are clearly working with the limited carbonate U-Pb standards available, the primary and secondary carbonate standards are far younger than the unknown sample (all over an order of magnitude younger than ALH 84001 carbonate). It would be beneficial to incorporate a discussion addressing potential uncertainties stemming from this and why they are (or are not) relevant to the conclusions herein.  
e.g. Are the effects of U-Pb fractionation (accounted for with measurements of WC-1) expected to differ for between younger and older material with different  $^{238}\text{U}/^{206}\text{Pb}$  ratios? This would fit in well with some of the pre-existing discussion on methodology in section 5.1.

Tartese & Lyon: The reference material are indeed younger than the carbonates in ALH 84001. This is very often the case for U-Pb dating in most mineral phases, e.g., zircon 91500 is a widely used primary standard and is *ca.* 1 Gyr-old. There is no obvious reason to think that U/Pb fractionation would vary according to the age of the dated phases.

### Line-by-Line Comments

**L 93-5** – Is this linear correction factor necessary or precedented? Are there alternative models and would these have an effect on the calculated dates? I have little expertise in the realm of SIMS U-Pb, so I apologize if this is a naive question.

Tartese & Lyon: This is indeed common practice for carbonate U-Pb dating by LA-ICP-MS. We have added a few words on this in the revised ms, together with references to Roberts et al. (2017), Drost et al. (2018), and Kylander-Clark (2020) [see also response to reviewer 2's suggestion on this].

**L 93,102** – Both regressions are stated as "anchored" and based on this phrasing and the shape of the uncertainty envelopes in Fig. S1, the authors seem to mean that they assume a fixed/anchored  $^{207}\text{Pb}$ - $^{206}\text{Pb}$  intercept for these regressions. I think the authors could be more explicit that they are assuming an initial Pb composition as their anchor. More importantly, the authors should justify the choice of this approach (over leaving the intercept a free-parameter in the regression) and comment on the appropriateness of the assumed initial Pb compositions and if these have any corresponding uncertainties.

Tartese & Lyon: This is correct, regressions for WC-1 and DBT are anchored at a fixed  $^{207}\text{Pb}/^{206}\text{Pb}$ , which have been precisely determined by Roberts et al. (2017) and Hill et al. (2016), respectively. So we are not assuming a common Pb isotope composition, we are using those derived from high precision analyses of these reference materials. These common  $^{207}\text{Pb}/^{206}\text{Pb}$  ratios are associated with small uncertainties that have been added in the revised ms. This is common practice for processing WC-1 data. For DBT data processing, it is hard to figure out if it is common practice to anchor the regression to the common  $^{207}\text{Pb}/^{206}\text{Pb}$  ratio of 0.74 as most studies only report the lower intercept dates they are getting, not whether the regressions are anchored or not [see also response to reviewer 2's suggestion on this].

**L 127** – This is an insightful result and I think the manuscript would benefit from some speculation as to why ALH 84001 carbonates inherited so little common Pb.

Tartese & Lyon: Without further direct analyses of the fluids from which these carbonates formed, it is hard to speculate further than saying that they likely contained very little lead.

**L 130-2** – The Rb-Sr and U-Pb inter-system concordance and resilience to resetting at 14 Ma is another insightful finding. I agree that this confirms that "not much happened" between these events (i.e. no further impact processing or aqueous alteration). I think the manuscript would benefit from some further discussion addressing what might have differed between impact events that did and did not effect carbonate system of ALH 84001.

Tartese & Lyon: We have expended the discussion in section 5.2 to include more discussion on these points.

**L 135-9** The potential application to CCs is exciting! The abundance of U in CCs is on the order of 10 ppb. Acetic acid leachates (Turner+ 2021, Science) of a CV and CM contain ~1ppm and 50 ppb U, respectively. It would be worthwhile for the authors to comment on the promise/challenge these present for *in situ* U-Pb dating of CC carbonates, compared to those of ALH 84001.

Tartese & Lyon: We agree with reviewer 1 that this potential avenue of research is exciting, and this is something we are looking forward to test. We have added a few sentences in the revised ms to expand a bit on this point, based on some of reviewer 1's suggestions.

**Fig. 2** – The authors do not explicitly identify the purpose of the bold black outline near 4000 Ma. Intuitively, this represents the confidence bounds on the mean date, but it would be helpful for readers to explicitly state that.

Tartese & Lyon: This has been added in the revised ms.

**Fig. 2** – Please identify whether these  $2\sigma$  uncertainties are standard deviation or standard error.

Tartese & Lyon: This has been added in the revised ms.

**Table S1** – The binning approach of the authors excludes the 300.8 Ma date of Drost+ 2018 in their compilation. While this does not effect their interpretations, I suggest the authors use bins without gaps between them for the tabulated compilation.

Tartese & Lyon: Thanks for pointing this out, this has been corrected in the revised Supplementary Table S1.

## Comment on gchron-2022-21

Anonymous Referee #2

Referee comment on "*In situ* U-Pb dating of 4 billion year old carbonates in martian meteorite Allan Hills 84001" by Romain Tartèse and Ian C. Lyon, *Geochronology Discuss.*, <https://doi.org/10.5194/gchron-2022-21-RC2>, 2022

### General comments

I appreciated the opportunity to read this interesting paper, which investigates carbonates within a Martian meteorite, Allan Hills 84001, using in-situ U-Pb LA-ICP-MS analysis. Previous work has identified the carbonates within this meteorite as forming in a low-temperature, near-surface aqueous environment (Halevy et al. 2011, del Real et al. 2016) from fluids that record clay weathering on a wet Mars (Beard et al. 2013) roughly contemporaneous with a major shock event recorded by ALH 84001 (Treiman 2021). These carbonates have been previously dated to  $3.94 \pm 0.02$  Ga by Rb-Sr and Pb-Pb analysis of carbonate following sequential leaching (Borg et al. 1999) and Rb-Sr analysis of mineral separates from carbonate-rich zones and a leach-residue pair of a carbonate-rich fragment (Beard et al. 2013). These data—clear evidence of an ancient, wet, cool Mars—are thus critical for understanding the paleoclimate and past habitability of Mars.

This study continues the investigation of ALH 84001 by directly dating these carbonates using the rapidly emerging technique of in situ U-Pb carbonate dating via LA-ICP-MS. The authors recover ages consistent with prior work within uncertainty. These data suggest that the U-Pb carbonate geochronometer can be viable over billions of years and indeed may be very suitable for dating carbonate from extraterrestrial bodies without a hydrologic cycle or tectonic activity (which add a great deal of complexity in the analysis of Earthbound carbonates). The authors highlight potential future applications to studies of the early solar system, and in their revision, I hope they will push farther about the application of this technique to these questions.

In this comment, I highlight some points of consideration here that I think the authors should address prior to publication of this work. I am not yet convinced that the carbonates analyzed contain no common Pb, as the authors suggest. In addition, I make some suggestions for the authors' consideration that I think will improve the analysis, clarity, and impact of their paper. Following revision considering these points, I believe this paper will be suitable for publication in *Geochronology*. Thanks once again to the editors and authors for the opportunity to engage with this work.

**Tartese & Lyon: We thank Referee #2 for their constructive and insightful review of our study. We explain below how we have addressed all their suggestions.**

### Specific comments

31: The authors have performed a useful service for the community by compiling previous carbonate U-Pb LA-ICP-MS studies in their supplementary table 1. Thank you!

**Tartese & Lyon: You are very welcome!**

53: Picking up on the quoted observation that there is little evidence anything happened to ALH 84001 from 3.9 Ga until launch from Mars c. 14 million years ago and subsequent deposition on Earth's surface: The fact that the authors recover a 3.9 Ga age from these rocks

also indicates that the carbonates within ALH 84001 were not reset by hydrological or weathering processes on Earth following launch. Given the perceived susceptibility of carbonates to dissolution and reprecipitation, it seems worth noting that ALH 84001 sat at or near Earth's surface for 14 million years and the U-Pb carbonate geochronometer was also not reset by these processes. This is likely a function of dry and cold conditions in Antarctica, but still worth noting. Indeed, results from Borg et al. 1999 suggest contamination by terrestrial Pb, rather than resetting of carbonate, is a greater concern for the reliability of dates generated from carbonates in ALH 84001.

Tartese & Lyon: ALH84001 has not been on Earth for 14 million years; it fell to Antarctica ~13,000 years ago (Eugster et al., 1997) and was buried deep in the ice, only coming to the surface probably no more than ~500 years ago (Krähenbühl et al., 1998). This has been specified in the revised ms, in which we have expanded the section on the geological history of ALH 84001.

95: The linear correction factor applied here is common practice in the U-Pb carbonate LA-ICP-MS community and it might be worth citing other examples of this practice from different labs, plus referencing Chew et al. 2014 and Roberts et al. 2017, which describe the procedure in more detail.

Tartese & Lyon: Good point, this has been added in the revised ms, together with references to Roberts et al. (2017), Drost et al. (2018), and Kylander-Clark (2020) [we did not include Chew et al. (2014) as it does not deal with carbonate U-Pb dating].

101: Is it common practice to anchor DBT? Anchoring WC-1 is common practice (and discussed at some length in Roberts et al. 2017, including a justification of the 0.85 value used here). I am not sure it is common to anchor DBT or secondary standards in general; certainly it seems to weaken the utility of these analyses as an accuracy check on the other analyses, which goes unmentioned on by the authors. The authors should provide additional discussion on this point and provide information on how the common Pb composition used for DBT was generated. If other studies routinely anchor DBT, the authors should cite them to demonstrate that this is common practice.

Tartese & Lyon: This is indeed common practice for processing WC-1 data. For DBT data processing, it is hard to figure out if it is common practice to anchor the regression to the common  $^{207}\text{Pb}/^{206}\text{Pb}$  ratio of 0.74 as most studies only report the lower intercept dates they are getting, not whether the regressions are anchored or not. This the common  $^{207}\text{Pb}/^{206}\text{Pb}$  ratio of  $0.74 \pm 0.02$  was calculated based on isotope dilution – MC-ICP-MS analyses of DBT presented in Hill et al. (2016) [see also response to reviewer 1's suggestion on this].

111: I was surprised to read that the carbonates analyzed contain no common Pb. As the authors note, this is quite unusual in terrestrial carbonates. The authors offer two lines of evidence:

- ALH 84001 carbonate analyses plot on the concordia curve, indicating that they do not contain an appreciable amount of common Pb.
- Measured  $^{204}\text{Pb}$  intensities are within error of zero.

I believe these points needs more attention from the authors and I look forward to their clarification in the case that I've misunderstood something.

- The analyses plot on and around concordia, but I am not sure that the analyses are sufficiently precise to make it clear if they are plotting **on** concordia or in a linear array **near** concordia. Can the authors rule either option out?

Tartese & Lyon: This is a fair point, uncertainties are fairly large for some of the analyses indeed. Looking at Fig. 2A, most analyses do plot on the concordia, and there does not seem to be any hint at a linear array. But again, small levels of discordance could be masked by relatively large uncertainties for some analyses.

- 202Hg counts during analysis of ALH 84001 are much higher than for other analyses (average of 907 during ALH 84001 versus 63 for all other analyses). Why is this? It suggests an analytical issue specific to the ALH 84001 sample. This has implications for the 204Pb\_corrected values shown in Table 1 and could have implications for other measurements on ALH 84001. The authors should discuss this, especially if they want to argue that ALH 84001 carbonates contain no common Pb.

Tartese & Lyon: The 202Hg and 204(Hg+Pb) counts for ALH 84001 carbonates are indeed a lot higher than those measured on terrestrial carbonate standards. All analyses were carried out during the same session, so this does not reflect extra Hg in the Ar gas during ablation of ALH 84001 carbonates. The first possibility is that ALH 84001 carbonates contain significant quantities of Hg – we think this is unlikely. The alternative is that some Hg contamination has been introduced to the sample somehow – secondary ion mass spectrometry investigations have been carried out in the past on the studied polished section, and we think that this extra Hg comes from Hg-contamination introduced by previous Au coating applied to the ALH 84001 sample. We have added some text on this in the revised ms.

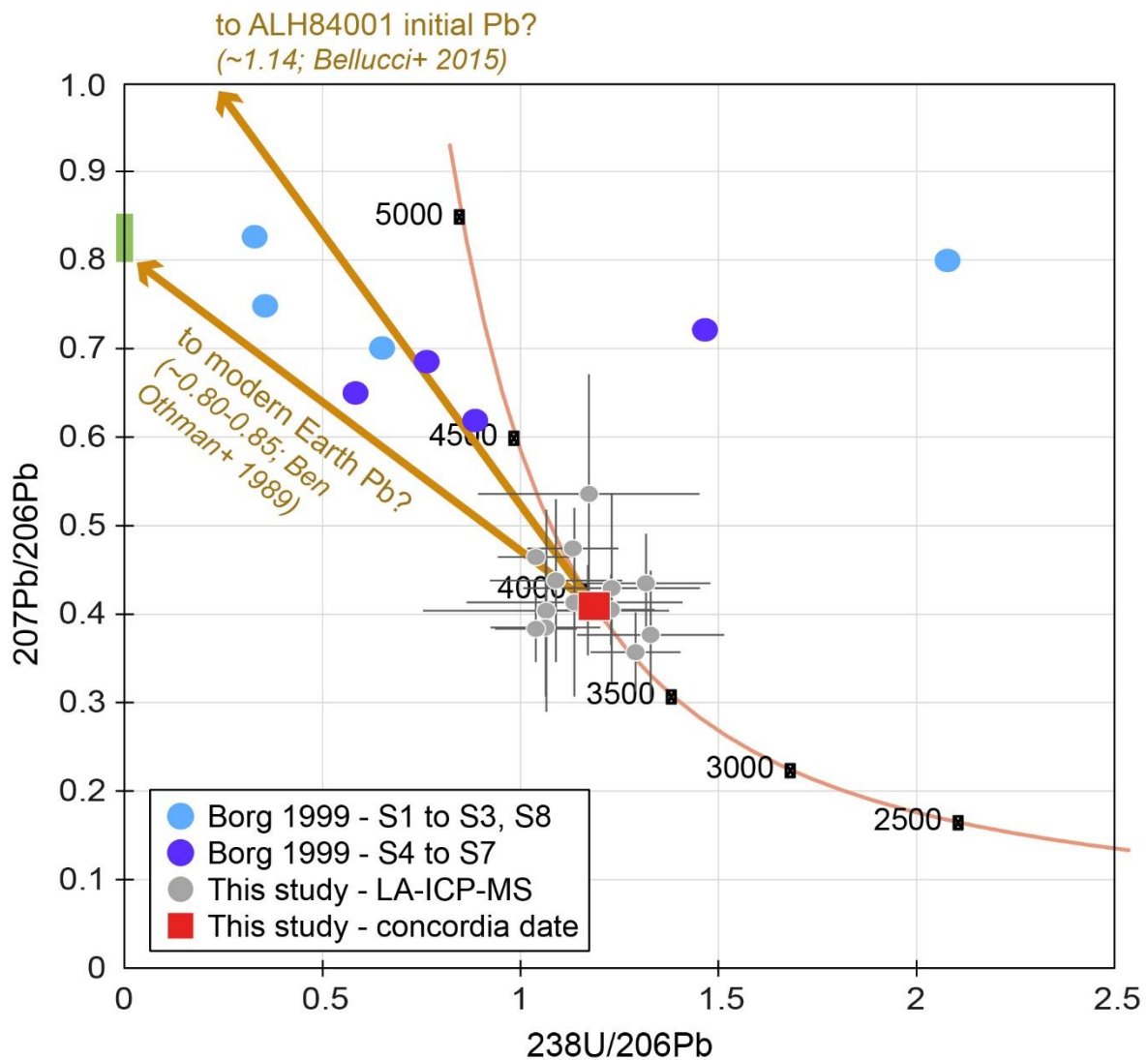
- Measured 204Pb intensities are within error of zero for all calcite standards analyzed, yet all these standards contain common Pb (e.g., WC-1 contains 85-98% radiogenic Pb), which is why they plot in linear arrays representing a mixture between common and radiogenic Pb. Therefore, measured 204Pb intensities being within error of zero is not good evidence of a common Pb-free carbonate in this analytical set-up. Naively, I'd think this means that the analyses were not sufficiently sensitive to resolve 204Pb in a meaningful way (which is often the case in LA-ICP-MS work). So the second point given by the authors above fails to convince me. Can the authors respond to this point?

Tartese & Lyon: This is a fair comment – although a few analyses of the DBT standard display calculated 204Pb intensities > 0 even when considering uncertainties, most of calculated 204Pb for the standards are within error of 0 counts/sec. On the other hand, NIST 612 analyses display ca. 600 c/s 204Pb corresponding to 0.5 ppm 204Pb, indicating that the abundances of 204Pb in all the carbonates analyses are a lot smaller. We have added a note in the revised ms to highlight the fact that this should be viewed as a qualitative assessment.

- How do the authors reconcile the idea that these carbonates contain no common Pb with the Pb-Pb results presented by Borg et al. 1999? Figure 3 of this paper shows an isochron formed by different carbonate leachates, all with varying 207Pb/204Pb and 208Pb/204Pb compositions. I would interpret their data as being consistent with low but extant common Pb in ALH 84001 carbonates, and I would be curious to read the authors' take on this previous dataset.

Tartese & Lyon: Borg et al. (1999) carried out stepwise dissolution followed by high precision U and Pb isotope analyses. Based on the elemental abundances of the different leachates, they tried to constrain which ones likely corresponded to carbonate fractions.

When plotted in a Tera-Wasserburg diagram (see figure below), 6 out of the 8 fractions analysed by Borg et al. (1999) plot to the left of the concordia curve, suggesting that these fractions contain non radiogenic Pb components. Interestingly, these fractions plot in a triangle between our calculated concordia date of ~3.94 Ga, the initial  $^{207}\text{Pb}/^{206}\text{Pb}$  of ALH 84001 (~1.14; Bellucci et al., 2015), and the modern terrestrial  $^{207}\text{Pb}/^{206}\text{Pb}$  isotopic composition (~0.80-0.85) of Ben Othman et al. (1989) used in Borg et al. (1999). This suggests that all these fractions contain a mixture of radiogenic, common martian, and common terrestrial Pb. This is perhaps not surprising that some terrestrial Pb contamination remains unavoidable when carrying out stepwise dissolution experiments on meteorites. On the other hand, our *in situ* method seems to be able to target specific areas largely free of non-radiogenic Pb contamination.



- If there is some fraction of common Pb present in ALH 84001 carbonates, this could complicate interpretation of the  $^{207}\text{Pb}/^{206}\text{Pb}$  ages presented here. The authors could



do some sensitivity testing of how much it would affect the age, given a range of common Pb fractions and compositions. I recommend that they do this.

Tartese & Lyon: If there was some common Pb in the ALH 84001 carbonates, this would indeed affect the calculated  $^{207}\text{Pb}/^{206}\text{Pb}$  dates, which would become younger and younger with increasing levels of common Pb. However, as discussed above, we do not see (within our uncertainties) any evidence for the presence of common Pb, and so haven't made any modifications on this point.

If the authors remain convinced that ALH84 carbonates contain no common Pb, I would ask that they speculate on why these carbonates contain no common Pb, and what about their environment of formation might be so different as to produce them. This might clarify the history of fluids and fluid-rock interaction on Mars.

Tartese & Lyon: Reviewer #1 made a similar suggestion that we speculate further on why ALH 84001 may contain very little common Pb, and what this could tell us on their formation environment. As mentioned in response to reviewer #1 suggestion, we find it hard to speculate further than saying that the fluids from which carbonates formed likely contained very little lead without further direct analyses of these fluids.

A paper the authors might find useful, on the limits of LA-ICP-MS in low-Pb carbonates: Kylander-Clark 2020 in *Geochronology*. I suggest that the authors add this paper, and the issues it raises, to their discussion. (It might also be helpful to compare the low-Pb carbonates written about there, and their environments of formation, to gain more insight into these ALH 84001 carbonates.)

Tartese & Lyon: We have added this relevant paper in the revised ms and refer to it the method description. Having read through this paper carefully a few times, we do not find much relevant information on low-Pb carbonates and their formation environments that we should be adding to our discussion.

123: It is good that the authors mention the fact that they have used a calcite reference material to correct for U-Pb fractionation in magnesite and ankerite carbonate matrices. I think it is worth noting earlier in the paper: that they are doing this; that matrix effects in LA-ICP-MS of carbonate are still not well-understood; and that no matrix-matched standard for magnesite and ankerite is available, rather than making only this short statement at the end of the paper. Further, although the results may be *consistent* with the idea that calcite standards can be used to correct for U-Pb fractionation in other carbonate matrices, this study was in fact not designed to test this idea outright, and all the secondary standards used in this study are calcite as well. So the statement as given here seems a bit too strong.

Tartese & Lyon: We have added a sentence on this in the methods section in the revised ms. Also, reviewer #2 is right that our study was not designed to assess potential matrix effects on U/Pb fractionation between calcite and magnesite-ankerite carbonates. The only observation we can make is that using a calcite RM does yield a U-Pb concordia date for ALH 84001 carbonates consistent with previous dating studies of these carbonates, implying that we can not detect any hint of variable matrix effects within our obtained uncertainties, as stated in the ms.

The authors group both Ca- and Mg-rich regions in their analysis as shown in Figure 2. It seems worth noting the similarity of the data from both regions, as at least some authors speculate that there were multiple water bodies involved in the precipitation of these carbonates (Treiman 2021).

**Tartese & Lyon:** We have added a sentence on this in the results section in the revised ms indeed, as this was also pointed out by reviewer #1.

Finally, I don't see a very large difference in Mg concentrations between the carbonates designated Ca-rich and Mg-rich when I plot the authors' data (see attached PDF). Is this expected? It might be helpful to highlight in figure 1 where spots were analyzed.

**Tartese & Lyon:** It is not immediately obvious from looking at the  $^{44}\text{Ca}$  and  $^{26}\text{Mg}$  signals indeed – our Mg-rich areas have an average ( $\pm\text{SD}$ )  $^{26}\text{Mg}/^{44}\text{Ca}$  ratio of  $18.1\pm 4.0$ , and the Ca-rich areas have an average ( $\pm\text{SD}$ )  $^{26}\text{Mg}/^{44}\text{Ca}$  ratio of  $10.4\pm 6.5$ .

130: It might be interesting to hear from the authors about the benefits of LA-ICP-MS for samples like theirs. Are the spatial resolution, speed, and less destructive measurements possible with LA-ICP-MS versus traditional solution work worth the trade-off for less precise dates, especially for the types of questions they identify at the end of their paper? I would be curious to read their thoughts.

Table 1: I feel it's essential to add the calcite standards used in this study (or at least, averages of them) to this table.

**Tartese & Lyon:** Data obtained on the calcite reference samples are provided in the Supplementary Table S3, and we do not think it's worth adding these to the Table 1.

### **Typographical comments**

70: 2 mL/min or 2 mL\*min<sup>-1</sup>

**Tartese & Lyon:** This has been corrected in the revised ms.

74: same issue as above on J\*cm<sup>2</sup>

**Tartese & Lyon:** This has been corrected in the revised ms.

76: same issue on elemental concentrations

**Tartese & Lyon:** This has been corrected in the revised ms.

126: terrestrial system carbonates (not systems)

**Tartese & Lyon:** This has been corrected in the revised ms.

216: superscript for U isotopes in citation

**Tartese & Lyon:** This has been corrected in the revised ms.

245: delta symbol for  $^{18}\text{O}$  in citation

**Tartese & Lyon:** This has been corrected in the revised ms.

Please also note the supplement to this comment:

<https://gchron.copernicus.org/preprints/gchron-2022-21/gchron-2022-21-RC2-supplement.pdf>

