Geochronology Discuss., author comment AC1
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Reply on RC1

Romain Tartèse and Ian C. Lyon

Author comment on "In situ U–Pb dating of 4 billion-year-old carbonates in the martian meteorite Allan Hills 84001" by Romain Tartèse and Ian C. Lyon, Geochronology Discuss., https://doi.org/10.5194/gchron-2022-21-AC1, 2022

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.,

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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 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 ± 72 Ma (2 sigma, MSWD conc. + equ. = 1.5, n = 8), while the Ca-rich carbonate analyses yield a concordia date of 3995 ± 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 will add 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 constructs an isochron, anchored at the WC-1 common 207Pb/206Pb 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 ± 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 238U/206Pb 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 will add 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 207Pb-206Pb 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 207Pb/206Pb, 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 207Pb/206Pb ratios are associated with small uncertainties that will be 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 207Pb/206Pb 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 will expend 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 will add 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 will be added in the revised ms.

Fig. 2 – Please identify whether these 2σ uncertainties are standard deviation or standard error.

Tartese & Lyon: This will be 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 will be corrected in the revised Supplementary Table S1.