Response to Reviewers are shown in Blue below

Review #2: New Developments in Incremental Heating Detrital 40Ar/39Ar Lithic (DARL) Geochronology using Icelandic River Sand, Okwueze et al. (2024).

Overview :

This contribution attempts to improve on the DARL method by overcoming the inherent limitations in previous applications that employed exclusively K-Ar methods. This is done using a detailed 40Ar/39Ar step heating approach. Much of the data are of high quality and show excellent release spectra. Data from some of the more complex step heating spectra are reasonably discussed.

Application of non-atmospheric trapped compositions for correcting plateau ages is also explained and justified. However, in the case of apparent non-atmospheric trapped components, I would use the isochron ages as these will be less affected by the trapped component issues.

The proposed method of 'partial fusion+averaged trapped component' is very poorly explained and it's implications are not clear. As read in the text, it appears to give a different, but similarly blurred picture of the age distribution of clastic materials as would the K-Ar method.

Most importantly, there is no raw data provided with the manuscript so age calculations cannot be verified or explored. **The manuscript cannot be accepted without this information.**

We thank you for your detailed review and expertise. The lack of supplements on the original submission was a major oversight and we have corrected it here.

Specific comments linked to line numbers:

73 : Use consistent units throughout (Ma).

All units switched to Ma.

77: Figure 1 - is low resolution and scale bars cannot be read.

Figure 1 edited slightly and exported at higher resolution.

126: Table 2 - Need to express to the precision to the correct number of significant digits, e.g., RHRDV01-4 : 0.42±0.23 Ma.

All significant digits fixed throughout text, figures and tables.

126 : Table 2 - Why are the plateau and isochron ages of RJKBR01-h so discordant? Especially considering the total fusion age is also older than the plateau.

This sample has very high atmosphere/radiogenic ratio (<3% radiogenic 40Ar % per step) and as such the isochron clusters near the atmosphere origin. Thus the isochron age has significant scatter. The total fusion age from this sample incorporates the highest temperature steps, which had excess argon and correspondingly much older apparent ages

(up to 14 Ma). However, the plateau still appears to be concordant with an atmospheric $^{40}Ar/^{36}Ar_0$ is employed, therefore the plateau age is preferred.

141: What does 'first order' mean in this context? Are you implying something about precision or accuracy requirements? I think this is important as it's at the heart of the matter – the balance between the data volume required by provenance studies versus the efforts to obtain the best precision and accuracy with the technique.

I agree that defining first order is important. I will also admit I overuse the term. I removed it in a few places. On line 252 I clarify that first order means lower precision: "which can provide a first order (e.g. low precision) assessment"

151: MSWD should be listed for both age spectra and isochrons. p for isochrons. Ages and uncertainties for isochrons.

Table 2 now has the MSWD, P, ages and uncertainties for spectra and isochrons listed. This information is also in the new supplemental document.

151: Since you discuss K/Ca below, it should be illustrated on the plots, along with an indication of the average (integrated) K/Ca that the reader can reference.

Added to each of the age determination result figures.

155 : Describe what the gray points are.

Added ", grey squares are excluded steps."

157 : Figures - Resolution is low making figures difficult to read. Needs to be brought up to publication quality. Could resize the isochron diagrams to be the same dimensions as the age spectra without consuming extra page space. The isochrons should be expanded (for example RHRDV01-b, RHRDV01-d or RPJRS01-a), that is, not plotted to the 39Ar/40Ar intercept, but rather to show maximum detail of the data and their relation to the regression line.

Should reconsider the scale on the age spectra. Most of the negative age range is unused and simply compresses the apparent scatter. Some plots, for example RJKBR01-g should be plotted on a finer scale as detail in the spectra cannot be seen.

All age determination results were cleaned up to increase clarity and add the desired K/Ca results. The apparent age scale bar was kept the same as -20 to 20 Ma to maintain clear comparison between the results. The supplemental document has all the necessary plots and the axes can be manipulated therein.

189 : "discordant plateau with steps in the same general age range...". A discordant plateau isn't really an age.

This is a fair point and the sentence was modified: "Out of the three grains that were analysed from the RSTDR01 sample (Stadará River), two produced concordant plateaus at ca. 13.4 Ma, and one produced a discordant plateau (Figure 3)."

193 : Confusing as written - the ages are not consistent with the proximal terrain, but instead the terrain that borders it. According to your watershed map, the lithic ages should not exceed 5.5 Ma. But this is an important observation; because you've produced age spectra, rather than K-Ar type ages, you can use these reliable dates to ask questions about what transport mechanisms could bring older detritus into this basin. If these were single-step fusions (i.e. K-Ar), you could simply dismiss them as having excess 40Ar. These older clasts effectively highlight why this is a much more robust approach.

This is an excellent observation. I have modified the sentence accordingly to capture your suggestion: "The RHRDV01 samples (Heradsvötn River) had three of four successful age determinations with two older (7.5 and 8.6 Ma) and one young (0.42 Ma) results (Figure 4). The older ages are not consistent with the currently proximal Pliocene-upper Miocene volcanic bedrock terrain (3.3-5.5 Ma) or the younger terrain upstream. These unexpected results highlight a strength of the incremental heating DARL method. Having the ability to obtain more robust age spectrums than traditional K/Ar or total fusion methods allows for more detail questions to be asked on sediment transport mechanisms as opposed to simply discarding unexpected outliers assuming excess 40Ar."

237 : I think you mean to say that K/Ca will be affected by various processes including, but not limited to, ...degree of source partial melting, etc.

Fixed accordingly: "The $^{40}Ar/^{39}Ar$ method provides a means of assessing the ratio of K (through $^{39}Ar_K$ proxy) to Ca ($^{37}Ar_{Ca}$), which can provide a first order (e.g. low precision) assessment of a variety of processes, including but not limited to, the degree of source melt enrichment, degree of mantle melting or the assimilation/crystal fractionation history of the sample."

241 : Surely at 1400°C the sample is fused and largely degassed. What does the 37Ar release curve look like?

Release curves added to figures 3 - 7. Some ^{37}Ar will keep being released at higher temperatures based on some unpublished experiments I've done. The 39Ar and 40Ar* are essentially done at 1400C.

245 : This comparison should be with bulk rock data since they would be equivalent to what you measured.

Fixed. The figure was modified accordingly. Figure caption: "Figure 9: The bulk rock K/Ca and alkali index values for known Icelandic volcanics. The K/Ca values for the analysed grains are shown as red bars on the y-axis. Icelandic sample data from the compiled GEOROC database (DIGIS Team, 2023) and filtered to K/Ca <1 to remove rhyolite samples. The alkali index is calculated as [Na2O + K2O] – [SiO2 x 0.369 - 14.350] (Rhodes et al., 2012)."

252 : Or you could simply split the grain, c.f., Ellis et al. 2017 https://doi.org/10.1016/j.chemgeo.2017.03.005

Option added. "Additional non-destructive (e.g. scanning electron microscopy [SEM] analyses), split grain (e.g. Ellis et al., 2017) or semi-destructive (e.g. laser ablation – inductively coupled plasma mass spectrometry [LA-ICPMS]) analyses prior to irradiation would be required to more thoroughly trace petrologic evolution"

254 : "This coupled petrological analysis and age determination on single..."

Fixed as suggested: "This coupled petrologic analysis and age determination on single grains would provide novel insights into the long-term first-order evolution of a volcanic terrain."

265 : Interesting point as you would then expect that using a non-atmospheric trapped component (as outlined below) should (could?) bias your ages relative the K-Ar ages in the literature which would have used an atmospheric correction.

Correct.

267 : You should show these in the table since you plot them in figure 8.

Added Table 3

275 : Do you mean temperature range? or a singular temperature? multiple steps?

Changed to "…temperature range"

278 : This should be in the table for reference

Added with Table 3

281 : Unclear what's being referred to here - do you mean t(0) regressions? Why would these be different as compared to a standard analysis? Why would the blanks be different? Because this is a single step? Please explain more carefully.

Expanded the sentence to further explain: "It is important to note that the partial fusion errors here are overestimated due to expected lower blank corrections (using a single preceding blank instead of a polynomial fit to multiple blanks) and peak regression uncertainties (higher peak signals released in a single heating step) during an actual fusion measurement."

282 : I'm not at all sure what you're proposing. Are you taking about fusing at a single temperature? Or doing steps only between 680-1140? What happens to the gas from the lower temperature steps? Do you discard it? Have you calculated how much time your method saves relative to a full step-heating experiment, especially as furnaces usually require high temp. burnout between samples?

To increase clarity on the recommended method we added the following:

“Based on these preliminary Icelandic results, our next recommended steps would be to pre-heat the grains to 680°C while under active vacuum, then perform a single 1140°C heating step to obtain the age of the grain. This will allow for 100s of grains to be analysed within a reasonable timeframe — providing the large N values needed for a detrital geochronology experiment. Alternatively, since the sensitivity to the sub atmospheric intercepts seems greater in the youngest samples, perhaps the alternate 40Ar/36Ar0 (296 ± 4) should only be used when a sample produces a negative age result.”

288 : Panel B should say "Partial fusion age calculated with..."

Good catch. Fixed.

288 : This sample in panel B, RHRDV01-b, becomes even less compatible with the upper age limits indicated by the watershed boundaries (5.5 Ma).

I concur the absolute age puts it further away but the larger uncertainties still remain within error of the original age.

288: You should put an actual 1:1 reference line in here for comparison. The line plotted here has no meaning.

A dashed line was added as a reference 1:1 line. The best fit line is still included as I believe it helps show that the partial fusion ages are a closer fit to the expected 1:1 result.

298 : Fifteen. 4 of them were rejected – at least that is what the table indicates.

Changed to “15 of 19”

Additional comments (recommendations, not requiring action for resubmission):

1) The approach could be significantly improved if the samples were pre-treated more rigorously, i.e., crushed, phenocrysts and alteration phases removed and remaining groundmass leached to obtain pristine groundmass fragments as is usual for basalt dating. Obviously clast sizes limit the amount of datable material that can be processed this way, but this pre-treatment will limit the interfering effects of alteration and excess argon in phenocrysts, making for more robust data. Having a smaller amount of high purity material is better.

I agree but the balance between mass available (e.g. 5-8mg per 2mm grain) and the age/nature of the samples (young basalts) make losing material difficult. We considered doing this on larger grains in the deposit but then would bias the results towards proximal deposits as lava flows are not robust like zircons during transport. The method definitely needs more refining and we had plans to run a series of variable acid leaching experiments on individual grains from the same lava flows (at variable sieve sizes) to obtain a best pretreatment plan. However, the nature of this project (undergraduate thesis) didn’t allow the time needed. I appreciate the recommendations for future investigations.

2) A CO2 laser-based approach would have lower blanks and can be run 24-7 for greater throughput. But even then, step-heating takes time.

I agree and that is the next step. The concern originally with using the laser was the grains are rounded and the laser will unevenly heat the large single masses. However, this is likely a minor effect (if any) and next we will use the CO_2 laser.

3) I think this approach will struggle to be applied as a high-N type of technique (like U/Pb zircon) because initial conditions and assumptions (initial daughter composition, closed system behaviour) have significant impacts and cannot easily assessed without detailed analysis. Single-step analysis will not alleviate this problem.

Although true, the alternative at this time is there are no options for detrital studies in mafic terrains. I believe some data with caveats is better than no attempts.

4) Assuming a 'regional' trapped component composition will only blur the picture of sample ages, giving this technique even less resolution.

As mentioned a few times in this response, the balance between accuracy and precision is key here. I rather have lower precision but a better chance of accuracy. If the we are dealing with a terrain like Iceland that has 15 m.y. of history then 0.5-1Ma uncertainties aren't the worst. But there is definitely room for improvement still. I also added the suggested alternative of using an alternative trapped component only for negative ages in the discussion.

5) A better approach would be to pre-screen the materials for key geochemical data and then use the geochemistry as guide to select grains for high precision and accuracy step-heating analysis. Step heating analysis is the greatest strength of the Ar/Ar method and so should be leveraged for maximum benefit.

This is ideal and suggested as part of the discussion. Screening is always a bit tricky as you have the potential to bias your results against certain lithologies that aren't ideal for 40Ar/39Ar (e.g. olivine rich rocks) but perhaps a defined set of 'red flags' that require the grain be step heated instead of fused could be employed.