Geochronology Discuss., author comment AC2
https://doi.org/10.5194/gchron-2021-41-AC2, 2022

Reply on RC1

Anthony Reid et al.

Author comment on "Complex ^{40}Ar□/□^{39}Ar age spectra from low-grade metamorphic rocks: resolving the input of detrital and metamorphic components in a case study from the Delamerian Orogen" by Anthony Reid et al., Geochronology Discuss., https://doi.org/10.5194/gchron-2021-41-AC2, 2022

Referee Comments 1 – Anonymous

Anonymous Referee #1, 21 Jan 2022

Reid et al. present new mineralogical and 40Ar/39Ar (furnace step-heating) data from fine grained, low-grade metamorphic rocks of the western Delamerian Orogeny, and use that data to distinguish between detrital and neoformed mica components. The data are also used to propose simple thermal history interpretations. The data are valuable, although the data presentation is incomplete, and I suggest that other interpretations can be reached, which have not been sufficiently explored.

My main concern is the 40Ar/39Ar data are interpreted solely considering combinations of the time of mica formation in a source region, the time of recrystallisation in the Delamerian Orogeny, and possible Ar loss via thermally driven diffusion during post-Delamerian tectonics. The logic behind the interpretation is accurate relative to these three issues. However, the authors should also consider the highly significant effects of secondary alteration, especially given the mineralogical data that is presented, which surprisingly is not considered in the interpretation section of the Ar isotope data. A robust approach would be to use mixing lines in ternary space to delineate, for example, between combinations of radiogenic 40Ar, 39Ar(K), 37Ar(Ca), 38Ar(Cl) (although unfortunately the samples were irradiated in a Cd-shielded position). These could be combined with the documented mineralogy (given the lack of microprobe data) to at least draw conclusions about which reservoirs are contributing to each heating step. This is fairly commonly done (e.g. see Challandes et al., 2008; Popov et al., 2019), and avoids ignoring fluid-related effects. E.g., were the protolith, Mesoproterozoic micas not altered at all between their original formation and deposition approximately 500 Ma later? Are the Delamerian-aged metamorphic micas unaltered? Has alteration reduced their age relative to their time of formation?

This is very helpful commentary. In addition to the York Plots, we have plotted 39Ar(K), 37Ar(Ca), 38Ar(Cl) and are interrogating what this might mean for the presence of alteration in the samples. A plot showing radiogenic 40Ar (*40Ar) is now included which shows the *40Ar for each step of the experiment. In addition, a ternary plot as suggested above has been made to be included. These analyses will be incorporated into the revised paper.

The 40Ar/39Ar methodology and data presentation are incomplete (see the recommendations in Schaen et al. (2021); https://doi.org/10.1130/B35560.1):

The methodology and data presentation that are recommended by Schaen et al 2021 are all addressed and available for our experiments. If these were not in the present supplementary data and/or within the paper, then that will be remedied. An electronic check list is available for this information and it will be included in the submission.

- *Line 174 reports that the samples were wrapped in Al foil, whereas line 481 reports they were wrapped in Sn foil.*

This is a misunderstanding can be easily fixed. The samples were wrapped in Al foils for irradiation, rewrapped in Sn to be analysed in the mass spectrometer.

- *Data tables are required for the analyses of the flux monitors and the K2S04 and CaF2 salts. Reid and Forster (2021) only provide data obtained from the samples.*

We can provide an excel sheet with the information on the flux monitors and the K2S04 and CaF2. This is not a problem. It is interesting to be asked for this as a number of labs do not analyse any salts but use the default values for these in their data reduction. However, yes our lab has this information available and we can include it.

- *How was the mass discrimination determined? Provide the values that were used so the dates can be calculated from the raw data by the reader. Were these dependent on ion beam intensity across the range of intensities measured ?*

We have accurate records of the calculation of the Mass Discrimination value. All the Air Shot data can be provided that relate to these samples. We do up to 5 Air Shots on each side of samples which are analysed in the furnace. All this information can be included in the submission. I have not seen other publications where significant detail has been included on this?

- *Which collector configuration was used (Argus VI), and what were the Faraday/CDD yields (if appropriate)?*

We have diverse ages of samples that are analysed in our laboratory, however we do not work with very young samples (e.g. rarely <1 Ma), so we use all Faraday Cups very successfully. Cross calibrations are done on the Faraday Cups regularly. We can provide this information in the submission, include a range of yields for these samples if that is required. We calculated the expected range of yield on each sample prior to their preparation, so as to maintain quality results from the mass spectrometer.

- *I gather from the text that the irradiation package included the flux monitors in a linear stack. What was the distance between each flux monitor?*

Yes, we have a glass tube and the foils are placed or stacked meticulously into the tube. Of course, we have details on the configuration of every irradiation, in this particular irradiation the samples were between flux monitors spaced at 6-7mm apart. For each of the flux monitor foils, between 5-8 separate analysis were done.

- *Provide a description of how the blanks for individual heating steps were determined once the sample was already loaded into the furnace crucible .*

All backgrounds are subtracted for every step. As the reviewer will be aware, blanks cannot be done once a sample is dropped as blanks are done on increasing temperatures which would not be possible. Blanks from the furnace are monitored carefully. Blanks are done to monitor the isotope levels prior to each sample for a range of temperatures from 350°C to 1450°C. A full set of blanks are repeated at the end to monitor changes. Blanks are also done in-between samples in a set if it is regarded necessary. All data are recorded.

Specific points

Introduction: The Introduction is clearly written although it would benefit from some more specific aims that are relevant for the Delamerian Orogeny. E.g., the info in line 108 would be useful in the Intro.

This can be incorporated.

Line 108: Where does this 480 Ma come from? The only previous reference to 480 Ma is in line 76 (Ar/Ar laser analysis of hornblende and biotite; Turner et al., 1996). Are the authors suggesting that the youngest of these Ar dates was previously taken to signal the end of orogenesis? The Ar dates are from granites so surely they just record cooling, and not crystallisation. U-Pb dates would be more reliable. Are there any? Line 69 suggests orogenesis was over at about 490 Ma.

This requires some clarification in the revision. The U-Pb dates are as young as c. 485 Ma, while the available $^{40}Ar/^{39}Ar$ dates are mostly around c. 480 Ma.

The Hylogger results presented in Appendix A require more clarity. As described in Appendix A, each sample is divided into a series of runs. For each sample, there are separate bands, each of which consists of three rows of coloured squares, which correspond to mineral compositions obtained by either SWIR or TIR. How should these three parallel rows be interpreted? Is each parallel row, one traverse such that each band of three parallel rows is three traverses? Or, is one band of three parallel rows, one traverse?

The HyLogger collects both SWIR and TIR data simultaneously. Therefore, the three rows of data presented for each sample in Appendix A relates to a single traverse and each sample was traversed five times. The three rows of data represent SWIR Mineral 1, SWIR Mineral 2 and TIR Mineral 1. However, we can see how this will be confusing for a reader unfamiliar with HyLogger data, so these Appendix figures will be edited to remove this part of the figure and simplify the results for the reader.

Furthermore, the colour for Mg-Chlorite is extremely similar (almost not distinguishable) from the colour for albite.

These are the standard colours used by the Geological Survey of South Australia and are

best viewed on screen in the Hylogger interpretation software. The colour for Albite and Chlorite-Mg are similar and the figures in Appendix A will be edited to ensure these colours do not appear adjacent to each other in the final presentation.

Lines 136 – 137. The TIR also shows a considerable amount of muscovite.

Yes, the TIR does also indicate muscovite in this sample, however depending on the mineral group, the spectral information is more definitive in one wavelength region compared to another depending on the particular absorption feature. Previous research has detailed the various bonds and overtones measured by the HyLogger. In this case, the Al-OH bond, represented by the 2,200 nm absorption feature, is well established in the literature to be the main diagnostic feature for white mica (muscovite/ phengite etc.). The absorption features for white mica in the TIR occur at approximately the same wavelength ranges as other mineral group absorption features such as various silicates (approx. 9,600 nm).

Typos in lines 129, 273, 319, 407

These will be fixed.

The plots in Fig 5 can be improved. Use the full space of the graphs. E.g. in 5a, modify the date axis to range between 200 and 650 Ma (the space between approx.. 750 Ma and 1200 Ma is currently blank).

All of the age spectra are on the same Y-axis scale to allow easy comparison between them. The reviewer's comment would mean that the different spectra could not be visually compared as easily and our preference is to leave the Y-axis at the same scale.

To help the reader, I suggest colour coding segments of the age spectra and York plots so the reader can match the topology of the spectra with specific trends in the York plots that are referred to in section 5. E.g. line 197. Which final steps, and which points are these on the York plot? Line 213 – which are the beginning and the final steps in the York plot? Etc……

We have updated software that colour codes the steps used. In addition this updated version also includes the errors on the York plot and step numbers can be included. This will be in the revision.

What is the author's definition of a minimum date? In some cases, the minimum date seems to be the 40Ar/39Ar date of the first heating step (e.g. 3779555), whereas in other cases the date of the lowest-T heating step is ignored (e.g. sample 3779551a). If significance is attached to a minimum date, then describe how the minimum date is defined.

We will go over the minimum date for each of the spectrum. We will define what this term means and keep a continuity in the use of the term.

Lines 240-242. Theoretically, a range in diffusion characteristics in a single crystal would yield a staircase spectra from a single crystal , depending on the t-T. However, complex age spectra can also be obtained from "single crystals" because they are frequently polycrystalline with perhaps several generations that arise by deuteric and low-T alteration (e.g. K-feldspar from the Chain of Ponds, Chafe et al., 2014; Klokken K-feldspar, Parsons et al. 2013; Itrongay K-feldspar, Popov et al., 2020; muscovite from Larderello, Italy, Bulle et al., 2020).

Yes, we agree with this. Comment on this will be incorporated.

Line 254. What do the authors mean by "main mineral gas reservoir"? Any combination of reservoirs that don't contain an initial component? There may be several radiogenic reservoirs if the grain is not 100% monomineralic.

This entire paragraph can be removed from the Discussion. Nevertheless, it is important to recognise however, that age spectra are the result of mixing between different gas reservoirs and in that sense all of the metrics collected in the step heating experiment are not "pure samples" of individual gas components. We will re-phrase this to make it clearer. It would read better as:

"An example of white mica from the South Cyclades Shear Zone, Ios, shows the initial heating steps having a distinct isotopic composition from the majority of the heating steps, representing a mixing between atmospheric and radiogenic gas compositions within the mineral separate (Forster and Lister, 2009)."

Lines 256 – 257. I realise this refers to previous work, but what is the justification for the statement that the older, high-T steps are infected with excess 40Ar? Could this also be inherited Ar from a xenocrystic component? More robust justification is required.

The York Plot for these samples shows the degree of mixing between atmospheric, radiogenic and excess argon, by definition. The steps we refer to plot towards the excess Ar composition on the York Plot. As indicated above, however, this entire paragraph can probably be removed from the Discussion.

Is 39Ar recoil evident in some age spectra? Several age spectra have a sudden reduction in date in the higher-T steps, followed by a subsequent increase in phyllite 3779553. Is this a recoil effect, which would not be surprising given the extremely fine grained nature of the groundmass? In this case, could the older dates (e.g. 709 Ma for sample 3779554) be artificially too old? Or, is a younger, more retentive phase being degassed? This should be addressed.

This is an interesting thought that could be considered due to the fine-grained nature of the samples. Where we do find recoil, it has been detected in the Arrhenius plot. In addition, a sudden change in %*40Ar can also have such an affect, and as we now include a plot of the *40Ar release across the experiment this can easily be seen if this is causing an effect as described here. This will be looked at in our revision.

I am not convinced that the 40Ar/39Ar date of 511±2 Ma (3779554) accurately records the timing of cleavage formation . Before making such a statement, the authors should demonstrate that this single heating step did not release Ar from any secondary alteration phases. This sample also hosts microcline, calcite and albite. E.g. did this step liberate any 37Ar from the calcite, and what was its influence on the 40Ar/39Ar date? Does this step contains and K released from the microcline? What is the relationship between the microcline and the foliation?

This is a fair comment. A more accurate statement would be that the 511 Ma age must be an upper limit on the timing of cleavage formation. The cleavage could have formed at that time, or sometime after. The c. 511 Ma age represents a limit on the age spectrum in the sense that the spectrum is a mixing between two or more age components in the rock.

The age spectrum is corrected for any interferences from interfering isotopes e.g. 37Ar, thus avoiding any effects of ^{37}Ar on the $^{40}Ar/^{39}Ar$ date.

Lines 314 – 324. Statements about the tectonic setting during deposition can only be

made if it can be confidently established that the oldest 40Ar/39Ar dates are accurate measurements of the age of the muscovite grains. This has not been demonstrated for all of the analysed samples. This process will always be best with U-Pb concordia ages, but it is less clear when 40Ar/39Ar (single step dates!) are used. I have no issue with the logic in this paragraph, although I suggest the authors at least acknowledge this, or make a more detailed comparison between any detrital zircon U-Pb data, and their oldest 40Ar/39Ar step dates. For example, did the Mesoproterozoic grains undergo any secondary alteration before they were deposited and captured in the Delamerian Orogeny? These statements should be addressed prior to making tectonic interpretations of single step-dates.

A modification to acknowledge the uncertainties in the interpretation will be incorporated.

Lines 337 – 359. The authors account for their Ar data by combining i) the time of growth/deformation, and ii) Ar loss by diffusion, which is subsequently related to exhumation. Given the mineralogy of the rocks (and the Hylogger analyses), the authors should also address the possibility of a reduction in date relative to the timing or deformation caused by fluid flow events that post-date Delamerian deformation. Could alteration be responsible for the reduction in date? If not, then why not, and use the available data to show this. The authors attach significance to the younger step-dates in sample 3779552. This sample hosts chlorite and albite, with a very low amount of muscovite. Could these younger dates simply be a result of secondary alteration? This should at least be addressed and a more robust justification is required to interpret the dates in terms of t-T paths, exhumation, fault reactivation .

Of all the samples, 3779552 is probably the best example of how alteration could be playing a role in the age profile. We acknowledge the submission did not adequately cover the likely effect of alteration and this can easily be incorporated into the revision.