

Geochronology Discuss., referee comment RC2
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Comment on gchron-2021-25

Anonymous Referee #2

Referee comment on "Direct dating of overprinting fluid systems in the Martabe epithermal gold deposit using highly retentive alunite" by Jack Muston et al., Geochronology Discuss., <https://doi.org/10.5194/gchron-2021-25-RC2>, 2021

General Comments

This manuscript describes temperature-controlled incremental heating $^{40}\text{Ar}/^{39}\text{Ar}$ results for ten samples of alunite (ideal endmember: $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$) from the Martabe epithermal Au deposit in Sumatra, Indonesia. While the quality of the language and figures in the paper is generally high, I have several concerns that range in severity from fundamental to minor with regards to the applicability of the results and the clarity with which topics are discussed. I will briefly summarize my chief concerns here, which are described in greater detail in the following sections of this review along with more moderate and minor concerns that mostly revolve around improving evidence for some ancillary interpretations (e.g., Cl contaminants hosted in fluid inclusions) and increasing the clarity of the paper.

First, the authors report using heating schedules starting at 450 C in all of their experiments, despite citing recently published work by Ren and Vasconcelos (2019) who demonstrated with ultra-high vacuum (UHV) transmission electron microscope experiments that alunite undergoes a structural transformation at temperatures of 430–460 C. Below these temperatures under UHV, alunite retains its natural crystal structure; but, above these temperatures, it becomes a polycrystalline aggregate with a potential change in structure due to dihydroxylation to $\text{KAl}(\text{SO})_4$ (alum) + Al_2O_3 aggregates. Ren and Vasconcelos documented an increase in activation energies and pre-exponential constants (e.g., $\ln(D_0/a^2)$) above this phase transition temperature (430–460 C), which can appear as upwards curvature on Arrhenius plots, and concluded that lower temperature data must be used to derive diffusion kinetics representative of natural alunite. Therefore, the results presented in this paper may not be relevant to the natural conditions of the Martabe epithermal Au deposit. Repeated experiments that include lower temperatures are required to evaluate this possibility for the Martabe sample set.

Second, the Fundamental Asymmetry Principle (FAP) is not described in the context of multi-domain diffusion (MDD) theory with sufficient clarity, and there is only a single statement noting a fundamental limitation of the method: that it cannot be applied in the

presence of microstructural changes. Because the results presented by the authors are all effectively at higher temperatures than the phase change documented by Ren and Vasconcelos, the data appear to follow expected MDD behavior in Arrhenius plots and the FAP was applied in analyzing the data. However, the authors also claim to have re-evaluated the results reported by Ren and Vasconcelos by applying the FAP, despite the documented phase change in alunite that is apparent in the Arrhenius plots of Ren and Vasconcelos as upwards curvature (due to increased activation energies at higher temperatures). Thus, by their own admission this appears to be an inappropriate application by the authors of the FAP in the presence of a microstructural change.

Third, the supplementary data and other materials were not made available to this reviewer, and no evidence was made available to evaluate how the authors reprocessed the results of Ren and Vasconcelos. This could have been due to mishandling of the supplementary materials, or perhaps the supplement was not submitted with the preprint. In either case, this severely limited my ability to evaluate claims that the closure temperatures the authors derived by reprocessing the data reported by Ren and Vasconcelos were in agreement with those reported by the authors. From my own calculations of closure temperature using the diffusive parameters reported by Ren and Vasconcelos (even for data above the phase transition temperature of alunite), I was unable to reproduce the high closure temperatures reported by the authors, which are generally higher than those of other authors (e.g., 150–300 C reported by Love et al., 1998, Landis et al., 2005, and Waltenberg, 2012). The lack of access to supplementary material also made it impossible to evaluate statistical methods (e.g., the handling of uncertainties when forming weighted means from data subsets with low degrees of freedom, the computation of 95% confidence intervals, regression methods, etc.) and whether the authors followed community data reporting standards (e.g., Renne et al., 2009; full reference: Renne, P.R. et al., 2009, Data reporting norms for $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology: *Quaternary Geochronology*, v. 4, p. 346–352, doi:10.1016/j.quageo.2009.06.005.). The general lack of clarity on statistical methods should be addressed, either by adding detail in the main text or supplement (if it is not there already), or by making more explicit reference to previous publications that provide sufficient descriptions of the statistics employed by the *eArgon* software used by the authors. I looked for publications describing the inner workings of *eArgon*, but could not readily find any; this software should not be a “black box” to the readers of this paper.

Finally, while the paper was purportedly focused on the hydrothermal history of the Martabe Au deposit, I found that the discussion was too heavily focused on experimental and analytical procedures. Indeed, by my count only about 333 words out of a total of 3683 (just under 10%) in the discussion section appear directly related to discussing the topic of the paper. While methods are important for this kind of work, there should be a larger fraction of the discussion section devoted to the Martabe deposit and implications for economic geology.

I was initially very excited to see this paper, and I believe it would be a great service to the community for high precision $^{40}\text{Ar}/^{39}\text{Ar}$ data and diffusion information to be reported for alunite from the Martabe epithermal Au deposit. However, in its present form, I believe this manuscript is not yet ready for publication in *Geochronology*. I strongly encourage the authors to perform additional experiments that include lower temperatures on the ten alunite samples from this preprint, followed by submission of a revised manuscript. With improved clarity (regarding MDD theory, statistical methods, caveats of the FAP, more

detailed analysis of asymptotes and limits without loss of interpretations of min/max ages, etc.) and careful application of the FAP (if and where appropriate), I think this kind of work would be an excellent contribution. I sincerely hope the authors find my comments to be constructive and helpful in generating a revised manuscript for resubmission.

Specific Comments

Comments by topic

For a paper focused on unravelling the history of hydrothermal activity at the Martabe epithermal Au deposit, there is surprisingly little discussion dedicated to this topic (only about 333 words out of a total of 3683 in the discussion section, or about 10%). Rather, most of the discussion section focuses on experimental and analytical methods, which, while they are important aspects of the current work, arguably should not take up 90% of the discussion. For example, can you expand your discussion of the geometry of the hydrothermal system? It is currently limited to a small portion of the 333 words in the final section of the discussion and a single figure (Fig. 14). What are the implications of understanding how hydrothermal activity migrated spatially over a 2 Ma period? Could this have impacted how the ore bodies formed, or provide any utility for vectoring to the ore body during exploration? What are some relevant economic geology interpretations that you can make from your dataset in addition to the timing of hydrothermal activity (e.g., how do grades of ore correlate with the hydrothermal activity)? How significant is it that you've identified pulses of activity over a roughly 2 Ma period? How confident are you in the timing of each of those pulses, given that you dropped min/max age interpretations when aggregating asymptote and limit dates into probability density plots? More discussion is warranted that is more directly related to the topic of the paper: the history of hydrothermal activity at the Martabe Au deposit.

Regarding the Fundamental Asymmetry Principal (FAP) given the context of other recent diffusion studies: it must be made more explicit early in the paper that the FAP is predicated on MDD situations (the presence of multiple diffusion domains in samples). Also, consider the work of Cassata et al., 2013 (Cassata, W.S., and Renne, P.R., 2013, Systematic variations of argon diffusion in feldspars and implications for thermochronometry: *Geochimica et Cosmochimica Acta*, v. 112, p. 251–287, doi:10.1016/j.gca.2013.02.030): they (and references they cite) observed Arrhenius data with upward curvature that would violate the FAP. Cassata et al. interpreted this as an effect of structural transitions in the mineral due to laboratory heating (e.g., thermal expansion which can occur on short timescales, and lattice deformation like the transition from triclinic to monoclinic that can pose an activation energy barrier and exhibit hysteresis on retrograde heating). These structural transformations combined with progressive exhaustion of sub-grain domains can cause non-linearity both downward (expected by MDD) and upward (not expected by MDD alone in most circumstances; see their Figs. 8 and 10 for examples). They included simulations of molecular dynamics coupled with diffusion modeling to arrive at this interpretation, among other lines of

evidence. Temperature-dependent anisotropy could also produce upward curvature (e.g., Huber et al., 2011; see Fig 4; full reference: Huber, C., Cassata, W.S., and Renne, P.R., 2011, A lattice Boltzmann model for noble gas diffusion in solids: The importance of domain shape and diffusive anisotropy and implications for thermochronometry: *Geochimica et Cosmochimica Acta*, v. 75, p. 2170–2186, doi:10.1016/j.gca.2011.01.039). You should be crystal clear about applicability of the FAP: it applies only in MDD situations where the contributions from structural transformations and temperature-dependent anisotropy are negligible. To be fair, you acknowledge this (lines 249–253) when you describe the FAP, though it is very easy to miss the operative qualifier (emphasized here in bold): “The Arrhenius plot can be analysed by the selection of lines that divide the population by rank order. Such dividing lines obey the Fundamental Asymmetry Principle (or FAP) recognised by Forster & Lister (2010) and allow estimates for the activation energy of individual diffusion domains. This is a mathematical result that must be applied if one assumes argon loss takes place only as the result of solid-state diffusion **without microstructural modification.**” Look again at the work of Ren and Vasconcelos (2019); they have multiple sections of their paper dedicated to describing the structural transformations in alunite as a result of laboratory heating, which they confirmed with TEM heating experiments in ultra-high vacuum (UHV) conditions. They found that a phase transformation occurs under UHV between 430–460 C, such that the alunite structure gives way to polycrystalline aggregates (of alunite or a mixture of alum + Al₂O₃ nanocrystalline aggregates). They observed that the activation energy of Ar diffusion increased above this phase transition, which appears as upward curvature with increasing temperature and would violate the FAP as stated in Forster & Lister (2010). Furthermore, you state that you started your incremental heating schedules at 450 C; this would imply that all of the diffusive parameters that you report are likely applicable to the post-phase transition polycrystalline aggregate produced when heating alunite above about 460 C. In a way this is good news because you would expect MDD behavior, consistent with the fact that none of the Arrhenius plots you show exhibit upward curvature that would violate the FAP. But it is bad news in the sense that the diffusive parameters you derived may not be related to crystalline alunite at temperatures relevant to epithermal systems such as the one at Martabe. Perhaps you started this work before the paper by Ren and Vasconcelos was published, so your heating schedules did not make allowance for the phase transformation they documented under UHV conditions. But their paper has been out for more than two years; at a minimum you should be forthright in stating the possibility that your current results might not represent crystalline alunite, and you should perform additional experiments that include lower temperatures in step heating schedules to evaluate if and when phase transitions occur in Martabe alunite (after all, compositional variations could influence the temperature at which alunite experiences a phase transformation under UHV conditions). But this should not be left to the readers’ imaginations; you should provide evidence. Also, you should be careful in applying the FAP to the results of Ren and Vasconcelos given that they documented a phase transformation that occurs part way through their experiments, and because of your own statement that the FAP “...must be applied if one assumes argon loss takes place only as the result of solid-state diffusion without microstructural modification.” Please see additional specific comments about your reassessment of the Ren and Vasconcelos results below (for lines 545–546).

Regarding the *eArgon* software: the analytical algorithms and statistical methods implemented in this software should be clearly exposed to the readers, either by explicit description in this paper or by reference to a paper that does include sufficient detail. At present, this software is effectively a black box. For example, do you have a publication analogous to that describing ArArCALC (Koppers, A.A.P., 2002, ArArCALC—software for ⁴⁰Ar/³⁹Ar age calculations: *Computers & Geosciences*, v. 28, p. 605–619, doi:10.1016/s0098-3004(01)00095-4)? Or maybe another paper where you describe

things like regression methods, handling of errors, outlier detection, and assessing goodness of fit? These details should be made readily available to readers.

Figures 3–12: potential for improved clarity: consider modifying captions and in-figure labels to use descriptive keywords indicating how you have identified spectrum segments with age significance (e.g., label them as min/max age, upward/downward-bounding asymptote, intermediate asymptote, etc.). You can cite your 2004 publication for detailed descriptions of the various asymptote types (probably in main text where you describe your methods), but I think it would be good to use consistent terminology with the method you developed (rather than “plateau segment”). Also, it would be nice to have the upper x-axis of Arrhenius plots labeled with temperature in Celsius; this would help potential readers who may not be familiar with such plots to interpret them more effectively (e.g., by seeing in plain text that higher temperatures are to the left).

Line-by-line comments

Lines 101–102: Did you also correct for decay of ^{39}Ar and/or ^{37}Ar following irradiation? Do you list what decay constants you used for that (e.g., in the supplement)?

Lines 105–108: Earlier (line 96) you mentioned picking a total mass of 100–150 mg per sample. Did you then analyze single grains, or did you analyze multi-grain aliquots? Please clarify in these lines.

Lines 113–114: You are injecting interpretation very early into the paper by identifying fluid inclusions as the carriers of KCl and CaCl_2 contaminants. I would recommend withholding interpretation until after the results are presented. Also, I have separate concerns about fluid inclusions as the hosts for contaminants that dominantly produce effects on Cl/K and Cl/Ca ratios at very high temperatures; see additional comments below (e.g., for lines 234–235).

Lines 145–146: The following statement seems unnecessary and is misleading: “The resultant age spectrum allows vastly more information to be ascertained than any laser spot analysis can provide.” This is perhaps true of an individual laser spot analysis ($N = 1$), but to make a fair comparison you should only consider a single ($N = 1$) step from an incremental release spectrum. Laser spot analyses are rarely conducted in isolation; rather large numbers (dozens, $N \gg 1$) of spot analyses are performed, which, when interpreted as an ensemble (like a full release spectrum consisting of tens of individual steps is), can be extremely useful in identifying multiple generations of materials in a single petrographic section. Rather than selling incremental heating as the only game in town, consider that the two methods—incremental heating and laser ablation—have

different strengths and weaknesses and can complement each other. The former method, when performed with precise temperature control (for which you advocate), can be paired with diffusion modeling to provide insight into grain/domain size distributions and mineral/chemical reservoirs that may represent multiple age components; but the inferred identities of the minerals/microchemical reservoirs that released gases throughout the experiment are linked with model assumptions rather than direct visual observation. Laser ablation, when many analyses are performed on a sample, allows precise targeting of textural domains and potentially individual phases (depending on grain size) while preserving petrographic context for later visual inspection, so there is less ambiguity of what material is dated. However, for fine-grained samples especially, the ablated volumes can represent mineral mixtures and so must be interpreted with care and ideally with the support of modeling (just as in the case for incremental heating experiments of multi-domain and/or polymineralic samples). The bottom line is that both methods can yield populations of apparent ages resulting from a mixture of gases from potentially distinct mineral/chemical reservoirs, which must be interpreted accordingly while accounting for the strengths and weaknesses of each technique and with care in selecting model assumptions (e.g., using independent chemical and petrographic observations). The combination of these techniques can be very powerful since the strengths of one can alleviate the shortcomings of the other. Furthermore, what is the advantage of denigrating laser ablation in this context? It does not provide relevant information for interpreting your dataset; rather, it distracts from the point you are trying to make. I recommend removing this comment.

Lines 234–235: Please provide additional detail for the interpretation that inclusions (specifically identified in lines 113–114 as fluid inclusions) bearing KCl and CaCl₂ caused the observed increase in Ca/K and Cl/K ratios at high temperatures (apparently >800 C in most cases). Most fluid inclusion work I've seen indicates that fluid inclusions decrepitate at much lower temperatures, i.e., <400 C. There may be some potential for variation in decrepitation temperatures based on entrapment pressures, but I've not heard of fluid inclusions remaining stable to >800 C, even in alunite. What alternative hypotheses can you propose? For example, Landis et al. (2005; reference: Landis, G.P., Snee, L.W., and Juliani, C., 2005, Evaluation of argon ages and integrity of fluid-inclusion compositions: stepwise noble gas heating experiments on 1.87 Ga alunite from Tapajós Province, Brazil: *Chemical Geology*, v. 215, p. 127–153, doi:10.1016/j.chemgeo.2004.06.036) studied noble and active gases in ca. 1.87 Ga alunite from Tapajós, Brazil, and they observed increased ³⁸Ar/³⁶Ar ratios between 500–700 C. Notably, fluid inclusions generally released gases below 300 C, then the alunite OH sites released gases at intermediate (300–500 C) temperatures, and the K-SO₄ tetrahedral sites dominated gas release above 500 C. They attributed the increased ³⁸Ar/³⁶Ar ratios to nuclear reactions (induced by thermal neutrons produced by the decay of U and Th) on ⁴¹K and both isotopes of trace Cl (up to several hundred ppm) present in the K-SO₄ sites. This would help explain the increased contribution from Cl-derived Ar at high temperatures; but perhaps such an explanation would not apply for such young alunite as you have analyzed since there is little time for accumulation of nucleogenic products... You would need to evaluate this possibility more for your samples (e.g., do you know what the Cl contents are of your samples?), but it should perhaps be included in your multiple working hypotheses until disproven. But, supposing the observed increases in Ca/K and Cl/K are not due to fluid inclusions nor neutron reactions on ⁴¹K and trace Cl; what other types of inclusions could then be carriers of Cl? Perhaps some sort of mica or clay mineral, which is not uncommon in hydrothermally altered rocks? Do you have independent petrographic observations that could help constrain a possible highly retentive carrier phase included in the alunite? What about the XRD data you mention? Could you (or did you) include it in the supplement? (The supplement was not available for review.) There is opportunity here for you to evaluate additional hypotheses for the observed spikes in Ca/K and Cl/K in your release

spectra. Perhaps you could include an additional discussion section to expand upon the implications of your results beyond the diffusive characteristics of Ar in alunite and the timing of hydrothermal alteration at the Martabe deposit. Supplemental information would be very helpful in narrowing down the field of possibilities.

Lines 235–236: “In many cases, early steps define the most retentive diffusion parameters for alunite.” How is it possible to have less retentive domains degas after more retentive ones (especially when using a prograde heating schedule)? Does that require the less retentive domains to be shielded/enclosed by more retentive domains? Once the more retentive domains are exhausted, how could you then recognize less retentive domains? Shouldn’t the diffusion be rate limited by the enclosing phase/domain? Or, perhaps the volume fraction of low-retentivity domains is much larger than those for more retentive domains? How does this work?

Lines 249–251: This is the first time in the main body of the text where you mention the Fundamental Asymmetry Principle (FAP), but it is not explicitly clear that it assumes MDD (multi-domain diffusion) behavior. Indeed, at this point in the paper, you have not explicitly mentioned or described the concept of MDD; it is not until a few lines later (line 255) that it is mentioned without definition of the acronym. It is not until the next section, around lines 281–293, that you reference work by Lovera et al. (1997) in the context of single-domain diffusion and then weakly describe MDD with a series of implicit references but no explicit definition. This is a severe lack of clarity for any readers that are not familiar with argon diffusion work in general, and MDD work in particular. However, this should be relatively straightforward to rectify; introduce the concept of MDD explicitly earlier in the paper. It might be appropriate to describe in one of your methods sections, e.g., where you describe your diffusion experiments (the MDD context would be helpful for understanding your choices in experimental methods, too).

Lines 281–293: There is an opportunity to improve clarity here. You cite Lovera et al. (1997) in describing how diffusion parameters are determined for a single diffusion domain. But then you move into discussing MDD scenarios without making this explicit to the reader; even as someone familiar with this kind of work this was confusing, so imagine how a reader that is not familiar with MDD theory might react. I suggest amending the sentence on line 285 to read something like: “There has been much debate around interpretation of Arrhenius data for samples with multiple diffusion domains (MDD).” If you would rather mention the concept of MDD elsewhere in this section, that is fine, but I think it is essential to set the context explicitly. As currently written, it is unclear from the description on lines 287–291 what the Fundamental Asymmetry Principle states. Read naively, the description following “Simply put...” seems more like an observation that data points may lie to the left and right of a line, but does not really state how to interpret such a situation. The final sentence then citing the FAP and uniformity/density of data in $1/T$ space as critical requirements for determining closure temperatures and running diffusion models therefore feels confusing. But, by making it explicit that you are talking about an MDD scenario and that the FAP is predicated on the idea that the progressive exhaustion of domains should impose a particular “behavior” for Arrhenius data and that it should govern how data are regressed to extract diffusive parameters would help the clarity of this section. The paragraph in your Forster and Lister (2010) paper where the FAP is introduced does a nice job of setting the context before describing how data should be regressed, it would be great to see that emulated here. However, you must also be clear of situations in which applying the FAP is inappropriate,

e.g., when there are structural changes to the crystal lattice; see other comments regarding this above and related to your reassessment of the data published by Ren and Vasconcelos.

Lines 302–303: Have you considered using a kernel density estimate (KDE) plot? This is in a sense what you have done by (arbitrarily) selecting $\sigma = 0.05$ Ma in panel b of Fig. 13; but an adaptive kernel based on the clustering of the data could be useful. For example, the DensityPlotter of Vermeesch (Vermeesch, P., 2012, On the visualisation of detrital age distributions: *Chemical Geology*, v. 312, p. 190–194, doi:10.1016/j.chemgeo.2012.04.021) uses the adaptive kernel of Botev et al. (Botev, Z.I., Grotowski, J.F., and Kroese, D.P., 2010, Kernel density estimation via diffusion: *The Annals of Statistics*, v. 38, p. 2916–2957, doi:10.1214/10-aos799), which is designed to best replicate the unknown generating function using observations (data) generated by that function. I doubt this would fundamentally change your discussion here, but is perhaps something you can consider for future work.

Lines 303–308: It seems that any interpretations of asymptotes and limits as min/max ages are lost when the data are aggregated into PDPs/KDEs in this way. Isn't the directionality implied by min/max ages important for interpreting when periods of alunite growth occurred at Martabe? Perhaps it would be better to plot all minimum ages in one color, all maximum ages in another color, and all intermediate asymptotes in a third color? This might change the inferences that can be drawn from the figure for the hydrothermal history at Martabe, since it would retain a sense of bounding ages. By treating each asymptote/limit date as a potentially valid age of alunite formation, I think you reduce the reliability of your age interpretations. This is perhaps what your previous reviewers were driving at by commenting on the definition of a plateau (e.g., lines 318–329). While I appreciate your contention that we (as a community) should develop ways to analyze and interpret complex release spectra (which I agree with), I don't think that justifies treating means of two or three steps as totally reliable (which is effectively what you've done by plotting them together on PDPs and picking out ages from the largest peaks formed by overlapping "frequently measured ages"). Rather, I recommend treating the asymptotes and limits you identify as bounding limits where appropriate (min/max ages), and then preserve that context throughout your analysis and interpretation of the timing of hydrothermal activity at Martabe.

Lines 545–546: "We have scaled [Ren and Vasconcelos'] diagrams and applied the FAP and obtained revised estimates for the activation energy are entirely consistent with our results." This statement referencing alunite Ar diffusion results published by Ren and Vasconcelos (2019) should be accompanied by figures demonstrating your reprocessing, at least in the supplement (which was not available for review). This statement is also a bit confusing; when you say you scaled their diagrams, do you mean you worked with images of the figures? They published all their data; did you instead replot their data and perform your own analysis? The former seems insufficient to demonstrate similar results, while the latter would be reasonable and could easily yield supporting figures that you could include in the supplement. Notably, the range of closure temperatures you report (400–560 C assuming cooling at 20 C/Ma) are significantly higher than those reported by Ren and Vasconcelos (ca. 240–270 assuming faster cooling at 100 C/Ma, which should yield higher closure temperatures than those for slower cooling rates). Even the results "above phase transformation" (APT) reported by Ren and Vasconcelos only yield closure temperatures as high as ca. 330 C assuming cooling at 100 C/Ma (from my own

calculations using their reported activation energies and pre-exponential constants for APT regressions). It is important to provide evidence that your analytical methods yield dramatically higher closure temperatures using the data of Ren and Vasconcelos, assuming that application of the FAP is appropriate to their dataset (which is probably not the case for their alunite data; see separate general and specific comments regarding the FAP). Does application of the FAP to their data imply that higher-temperature steps (e.g., those they state are above the phase transition temperature) would be included in the regression of diffusion parameters on an Arrhenius plot?

Lines 561–562: The following statement seems unrealistic: “This is the first example of overprinting events being recorded in a single step-heating experiment of alunite.” Any release spectrum produced from alunite with classical signs of partial diffusive loss (i.e., younger apparent ages in the early steps of a spectrum) could indicate either slow cooling or later thermal overprinting. Are there really no such examples in the published literature? See for example Fig. 11 of Juliani et al. (Juliani, C., Rye, R.O., Nunes, C.M.D., Snee, L.W., Silva, R.H.C., Monteiro, L.V.S., Bettencourt, J.S., Neumann, R., and Neto, A.A., 2005, Paleoproterozoic high-sulfidation mineralization in the Tapajós gold province, Amazonian Craton, Brazil: geology, mineralogy, alunite argon age, and stable-isotope constraints: *Chemical Geology*, v. 215, p. 95–125, doi:10.1016/j.chemgeo.2004.06.035). I would recommend dropping this claim, but if you would like, perhaps it would be more appropriate to state this is the first application of the method of asymptotes and limits and the FAP in dating alunite with complex release spectra produced by thermal overprinting?

Lines 345–355: While I understand your position that temperature control is essential for diffusion experiments that are coupled with $^{40}\text{Ar}/^{39}\text{Ar}$ dating, I feel like this section is unnecessarily focused on semantics. Why should experiments that employ lasers to degas the samples but that lack precise temperature control not be called step-heating experiments? After all, the laser power output *is* controlled, and in general the laser power is increased from one step to the next (i.e., in a stepwise fashion) such that the temperature the sample experiences does indeed increase with each successive step. The temperature is simply not measured, and specific target temperatures are not specified. For many (if not most) applications, this is sufficient to assess a precise age for a well-behaved sample (e.g., one that had a simple thermal history and behaves as a single diffusion domain). But, as you point out, this is not sufficient for deriving diffusion parameters from a sample; temperature control is required in this case. I don’t think anyone argues with that. So why the comments on terminology? This feels more like an unnecessary distraction, and it takes up valuable space in your discussion section that could perhaps be better allocated to direct discussion of the economic geology implications of your dataset with regards to the Martabe Au deposit. I suggest eliminating this paragraph to reallocate discussion space, or at a minimum tone this section down to focus on fundamental issues (like the need for temperature control for diffusion experiments) rather than semantics (like what should or should not be called a step-heating experiment).

Lines 374–376: when you say you chose sample sizes that would allow enough steps at appropriate temp intervals, does this mean there are aliquots with multiple grains that you degassed? Or were all analyses conducted on single grains? Please provide more detail for clarity.

Lines 388–390: You again mention the presence of KCl and CaCl₂ impurities hosted by inclusions. I think you need more support for this interpretation, or at least some additional working hypotheses that can be tested. Wouldn't KCl impurities leave the Cl/K ratio constant? (Suppose only KCl was present as an impurity.) How can fluid inclusions survive to such high temperatures?

Lines 408–418: This paragraph is somewhat confusing to me given the context that you have effectively ignored the structural transition that alunite experiences during laboratory heating, as documented by Ren and Vasconcelos (2019; see additional general and specific comments above). Am I right that your argument here is that: (1) it doesn't matter what the diffusion parameters are or whether they apply to the natural epithermal hydrothermal system as long as (2) diffusion parameters for each inferred diffusion domain correspond to an asymptote or limit identified in the release spectrum, which therefore implies that (3) each diffusion domain is the result of a distinct period of alunite growth? If assertion (1) is true, then why bother reporting closure temperatures and interpreting the relative retentivity as a bonus for preserving ⁴⁰Ar/³⁹Ar systematics in hydrothermal alunite? Should you therefore omit such information from your paper? If assertion (2) is true, then why are there visible mismatches in the steps used to determine diffusion parameters and asymptotes/limits in release spectra in Figs. 2–13? For example, in Fig. 10 (chosen at random), there appear to be two domains defined in Arrhenius space using steps 7–11 and steps 17–21, but the corresponding dates inferred from the release spectrum involve steps 11–14 and steps 21–22. You have not explained this anywhere in the text as far as I can tell; perhaps that mismatch is expected. But it should probably not be left to the readers' imaginations; please explain more clearly. And finally, for assertion (3) do you have any independent evidence to suggest that the sub-grain domains present in alunite from Martabe grew at different times? It seems like classic optical petrography or some SEM/EPMA/EBSD work would go a long way in supporting such an interpretation. How can you rule out recrystallization during repeated hydrothermal events? And when you consider that laboratory heating under UHV conditions does cause structural modification of alunite (as documented by Ren and Vasconcelos), how does that affect this discussion? You've apparently admitted (perhaps unintentionally) that the diffusion parameters you've derived are not representative of the natural epithermal environment. But what then is the utility of your results for Martabe alunite? Perhaps age information for multiple episodes of hydrothermal alunite growth can persist during laboratory heating, but I think this could be discussed with more clarity and would benefit from independent evidence (e.g., petrography and SEM or similar work). And if you want to report closure temperatures for Ar in alunite that are relevant to natural environments, I again recommend that you perform additional experiments that include lower temperatures so that you can regress data from below the phase transition temperature of alunite (as recommended by Ren and Vasconcelos, 2019).

Lines 426–427: This is a reasonable statement given the context of studying microstructural domains that are well below the footprint/spot size of a laser system. But, as with your comment on lines 145–146, I do not understand the need for this statement. I don't think anyone would argue that diffusion information can be obtained by laser ablation when the diffusion domain size is so small, so singling out this technique feels more like an unnecessary distraction than a useful piece of information. I suggest removing this comment.

Lines 455–459: Again, what independent evidence is there for KCl and CaCl₂ salts (besides

the Cl/K and Cl/Ca ratios)? The high temperatures at which the Cl/K and Cl/Ca ratios abruptly change seems too high for fluid inclusion hosts, so where is the contamination hosted in the mineral? What other possibilities are there? See more detailed comments above for lines 234–235.

Lines 474–476: You make the statement “...the Frequently Measured Ages (FMAs) that have been recognised using Gaussian probability plots can be shown to be statistically significant using Poisson statistics: it is highly improbable that coincidences in the determined ages are the result of random processes.” Is this evidence shown in the supplement (which was not accessible for review)? If it can be shown, can you please show it? It may seem trivial to you, but as written this point this is effectively an unsubstantiated claim that limits transparency to readers.

Lines 547–549: “In review, we were asked to comment on the difference between [Ren and Vasconcelos’] spectra and our own. There is no reason to do this. Perhaps the flat spectra obtained by these authors imply nothing more than that only one generation of crystal growth took place in their samples?” I do not think this is such an outlandish request, especially for readers who do not themselves perform diffusion experiments. Is there a difference in the heating schedules you used compared to the work of Ren and Vasconcelos? Could that contribute to the appearance of the release spectrum? Or is it a geological difference that contributes to the differences? I find it totally reasonable that you could guide the readers through that thought process, at least to provide some direction so they can evaluate the spectra for themselves for effectively.

Technical Comments

The abstract reports activation energies in units of kJ/mol, but in figures units are given in kcal/mol. Please be consistent throughout the paper.

Section 2 appears to be missing; there is a section 1 (the introduction), and section 3 (where experimental and analytical methods are described). Please renumber sections.

Regarding the term “York Plot”: three-isotope correlation diagrams are in wide use in isotope geochemistry. With regards to $^{40}\text{Ar}/^{39}\text{Ar}$ work, diagrams of $^{40}\text{Ar}/^{36}\text{Ar}$ vs. $^{39}\text{Ar}/^{36}\text{Ar}$ were first used by Craig Merrihue and Grenville Turner (1966); later, Turner introduced a plot of $^{36}\text{Ar}/^{40}\text{Ar}$ vs. $^{39}\text{Ar}/^{40}\text{Ar}$ (1971). These later became commonly known as “normal” and “inverse” isochron plots, respectively. Besides developing a robust linear regression method that accounts for errors in both axes and error correlations, I’m not sure how involved Derek York was in developing or using plots of $^{36}\text{Ar}/^{40}\text{Ar}$ vs. $^{39}\text{Ar}/^{40}\text{Ar}$. If you prefer not to use the term “inverse isochron” because you feel it carries too many

interpretive connotations, perhaps falling back to the term “three-isotope correlation diagram” would be more appropriate and generic? Or perhaps call it a “Turner Plot”? Yes, the York regression is well known and commonly used; but the diagrams themselves should perhaps be considered separately from the regression methods applied in those data spaces. This is mostly a matter of personal preference; in the end, just be clear in defining the term that you use (preferably define it early and explicitly).

Figure 11e: The x-axis label appears to be malformed; should this read “Percentage ^{39}Ar released” like the other figures?

Line 65: Suggestion for usage of future tense; you state that your “... study *will build* on [the results of Sutupo et al., 2013]...” (my emphasis in italics). Consider saying “builds” or “has built”; the latter is perhaps most correct, as you have already done the work, and are reporting on it. Future tense is least appropriate as you are no longer planning to do the work.

Line 140: Consider a more active voice, e.g., “Using the [method of] ‘asymptotes and limits’ we were able to extract relevant age information...”

Line 150: The reference “Forster et al., 2019” appears to be a duplicate. When looking in the references section, I found both “Forster, M., Koudashev, O., Nie, R., Yeung, S., and Lister, G.: 40Ar/39Ar thermochronology in the Ios basement terrane resolves the tectonic significance of the South Cyclades Shear Zone. Geological Society, London, Special Publications, 487, 291-313, <https://doi.org/10.1144/SP487-2018-169>, 2019” and “Forster, M., Koudashev, O., Nie, R., Yeung, S., Lister, G.: 40Ar/39Ar thermochronology in the Ios basement terrane resolves the tectonic significance of the South Cyclades Shear Zone. Geological Society, London, Special Publications 487, 291-313, <https://doi.org/10.1144/SP487-2018-169>, 2020.” The publication date appears to differ when following the DOI link and selecting the Lyell Collection (2019) or GeoScienceWorld (2020). I recommend choosing one or the other, but do not include both; probably the earlier publication date would be more appropriate.

Line 229: Duplicate wording: “... towards a towards a...”

Lines 230–231: Suggestion for wording/punctuation: change “... because of mixing with a KCl/CaCl₂ gas reservoir derived from inclusions (?)” to “... potentially due to mixing with a KCl/CaCl₂ gas reservoir derived from inclusions.” The parenthetical question mark seems to indicate this is a potential interpretation, but also makes it seem like you are unsure of the statement rather than proposing a possible cause. Also, on lines 234–235 you reinforce this interpretation based on your observation of higher Ca/K and Cl/K ratios, so the question mark is a bit confusing.

Line 266: Consider use of active voice; instead of "To demonstrate the significance of the ages obtained, it was necessary to evaluate..." consider writing "To demonstrate the significance of the ages obtained, we evaluated..."

Line 283: Probable misspelling/wrong word; "paraments" should likely be "parameters".

Lines 289–293: Possible grammatical improvements for clarity (**in bold**): "Simply put, **the** line used to estimate diffusion parameters must divide the sequence of steps in the Arrhenius plot by rank order. Points of a higher rank order will lie on or to the left of the line and points with a lower rank order will lie on or to the right of the line. The FAP and the need to well populate the Arrhenius plots particularly in the lower temperature of the experiment is absolutely critical in gaining closure temperature data and in allowing modelling."

Lines 464–465: "... two orders of magnitude of more..." should likely be "... two orders of magnitude or more..."