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Interactive comment on "Potassium isotopic variability and implications for ^{40}K-based geochronology" *by* Leah E. Morgan et al.

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General Comments

This manuscript is a timely contribution to the literature – interest in K isotope variability is expanding, and the ^{40}Ar/^{39}Ar community is increasingly pushing for improved traceability and precision. Potassium isotope variability has been long neglected – and with good reason – but this manuscript represents a timely contribution to the literature and is a good fit in *Geochronology*.

As I detail below, it is disappointing that the result in the manuscript is based on using one of the lesser used calibrations of ^{40}Ar/^{39}Ar geochronology and note that this one result (which is the only result in this manuscript) has already been published – albeit in shorter form – by Morgan et al. (2018). Fortunately, it should be straightforward for the effects of K isotope variability on the more relevant calibrations to be presented in a revised manuscript, so I don't think this is a serious problem.

The manuscript is not clear on how crucial quantities are calculated – in particular how δ^{41}K are converted to ^{41}K/K or ^{41}K/^{39}K. This problem is detailed below. These quantities are not tabulated, nor are the most other quantities in the manuscript. This makes the current draft difficult to read and hard to reproduce but it is an easy fix.

I hope to see a revised draft of this manuscript published in *Geochronology* and thank the author for bringing this issue to the attention of the geochronological community.

Specific Comments

Why is only one type of ^{40}Ar/^{39}Ar calibration described?

As clearly stated in the manuscript, flux monitor calibration via a primary K-Ar reference material is only one way that that the monitor can be calibrated. This provides the most straightforward and most easily metrologically traceable calibration, but it is probably the least popular calibration at the present for high precision ^{40}Ar/^{39}Ar measurements and hasn't been for quite some time. Both astronomical calibrations (e.g., Kuiper et al., Rivera et al.) and U-Pb calibrations (Renne et al. 2010/11) offer higher precision calibrations and are far more popular for high precision ^{40}Ar/^{39}Ar work.

The author of the manuscript is obviously aware of this(!), but it's not clear why the effect of variable ^{40}K/K are not also calculated for the far more popular and relevant calibrations. The few labs that use a primary calibration of GA1550 are probably not approaching limits of precision defined by K isotope variability and are unlikely to be interested in this result.

It's unclear to me why the more popular calibrations haven't been used here. If the resulting variation is tiny, that's also an important result.

I should also point out that this result – the effect of K isotope variability on GA1550 calibrated FCs – was already published by Morgan et al. (2018) in the top paragraph of page 185 of that paper. This result seems to be the main conclusion of the current manuscript and it's not clear that the relatively minor addition of the calculations is a significant advancement on the previously published result, by the same author.

I strongly recommend that

1. The effect of variable $^{40}K/K$ is calculated for one or both of astronomically calibrated and U-Pb calibrated $^{40}Ar/^{39}Ar$.

How are $^{40}K/K$ and atomic weights derived?

The manuscript is rather unclear as to how it calculates the ^{40}K relative isotopic abundance. The manuscript uses measurements of the $^{41}K/^{39}K$, relative to SRM 999b ($\delta^{41}K$). Via the measurements in Morgan et al. (2018), these can then be traced to SRM 985, which have a primary gravimetric calibration published by Garner et al. (1975). The ^{40}K abundance (denoted $^{40}K/K$ in the manuscript) is equal to the molar $^{40}K/(^{39}K+^{40}K+^{41}K)$, and by dividing by ^{40}K is related to the isotope ratios via $^{40}K/K = 1/(1+(^{39}K/^{40}K)+(^{41}K/^{40}K))$. In the absence of new ^{40}K measurements (relative to ^{39}K or ^{41}K), one way (perhaps the only way?) to obtain an estimate of $^{40}K/K$ is to use the Garner et al. (1975) estimate for $^{41}K/^{39}K$ of SRM 985, and through the delta-experiment traceability chain, calculate the $^{41}K/^{39}K$ for the material of interest, assume a particular fractionation model (e.g., power law, exponential law etc.), and then calculate the $^{40}K/^{39}K$ (or equivalently, the $^{40}K/^{41}K$) from the degree of fractionation measured by the delta-experiments and the fractionation law.

The manuscript employs ratios of $^{40}K/K$ (e.g., $^{40}K/K^{garner}/^{40}K/K^{new}$) and constructs equations for decay constants and ages for flux monitors and standards using this ratio (denoted "r" in the paper). It might be assumed that the manuscript calculates

^{40}K/K, but it is not made clear. What I suspect that has been done is that they have assumed that the magnitude of the fractionation of ^{40}K/^{39}K (hopefully relative to SRM 985 and not SRM 999b?) is half of what has been measured for ^{41}K/^{39}K – effectively assuming a linear fractionation law (which is not an appropriate fractionation law, but is probably close enough). The manuscript then probably also makes the assumption that the magnitude of the fractionation in delta space is the same as the fractionation in "fraction" space, e.g.,

(^{40}K/^{39}Kmeasured/^{40}K/^{39}Kgarner – 1) = (^{40}K/Kmeasured/^{40}K/Kgarner – 1)

This equality is approximately true if ^{40}K/^{39}K and ^{40}K/K are very small, but it should be noted in the manuscript that this is not exactly correct and is more significantly wrong for larger ratios such as ^{41}K/^{39}K (where a 1 ‰ in delta space is 0.067 ‰ in fraction space).

A similar lack of clarity applies to the calculation of the atomic weight. An atomic weight requires knowledge of the relative isotope abundances of all the isotopes in a sample and will change if the isotope composition changes. Potassium-40 has a very small influence on the atomic weight (it adds $\sim$ 120 ppm) so changes in its relative abundance can be ignored (as was done in Morgan et al., (2018)), but each distinct isotope composition used should have its own atomic weight. The calculation is not described, nor are the calculated quantities.

I understand that some of the effort expended to use ^{40}K/K "ratio ratios" was so that the decay constants can be adjusted from published values, and that they do not need to be calculated anew. This is quite clever, and eminently reasonable. But the full K isotope compositions used should be written in the text or tabulated so that the calculations can be reproduced. With all the sleuthing necessary to work out what has been done, and apparent shortcuts taken via approximations, it is extraordinarily difficult to reproduce the calculations because the quantities of interest are never tabulated. Tabulating the results is straightforward, because we know what the Garner et al. (1975) ^{40}K/K value is (0.01167), and the manuscript at some point has calculated the difference between the ^{40}K/K of a sample and the ^{40}K/K of SRM 999b (which is traceable to SRM 985, from which the Garner et al. quantities are derived).

So to summarize, the manuscript would benefit from:

1. Detailing quantitatively, using equations, how to go from δ ^{41}K (relative to SRM 999b) to ^{40}K/K, or even better, ^{41}K/^{39}K and ^{40}K/^{39}K) and how to calculate the atomic weight.
2. Tabulating the ^{40}K/K (or even better, ^{41}K/^{39}K and ^{40}K/^{39}K) and atomic weights used in the calculations.

Generalizability of results

The manuscript is quite short, which is admirable, but since it's only applied to a single calibration, and a sample of a single age, it's difficult for readers to know how this might apply to samples of other ages. It would be useful to include a wider range of sample ages (alongside other calibrations).

The results (e.g., figure 2) are couched in terms of "bias" , considering extreme values. In my opinion, it would be far more useful if the distribution of ^{40}K/K was calculated, and a probabilistic result was presented. In other words, treating this as an uncertainty in the ^{40}K/K and propagating that uncertainty onto the age results. A very close analogy is the effect of variable ^{238}U/^{235}U in U-Pb geochronology, and Fig 2 from Hiess et al. (2012; Science v335 p1610), where the bias as a function of time is plotted, with a band representing the variability in 238/235.

I appreciate that this is extra work for the author, but a straightforward MonteCarlo error propagation can easily be done in most software packages (even excel) in a few minutes – there is no need to derive cumbersome error propagation equations. This would expand the generality of this manuscript enormously and benefit anyone not dating something that is 28 Ma.

The magnitude of the variability in age associated with $^{40}K/K$ variability should be compared to other systematic uncertainties. Is the decay constant uncertainty large or smaller? Is flux monitor age uncertainty larger or smaller? This will give non-specialists a sense of whether this is a first or second order problem to tackle.

Technical Corrections

The (approximate) isotope composition of K should be described in the introduction for a reader who is not intimately familiar with isotopes of K.

The Merrihue and Turner reference in the first paragraph is confusing because the placement implies that this is the reference for the half life, and not for $^{40}Ar/^{39}Ar$ geochronology. It might be worthwhile substituting a more general reference, like Harrison and McDougal, that encompasses both.

I think that at this point in geochronology Steiger and Jager is not really a good reference for decay rates and branching ratios. It describes an agreed "convention" and doesn't detail how the quantities were compiled or derived. Beckinsale and Gale or Min et al. are probably more appropriate. Or Renne et al. (2010/2011) if you really want to stir the pot.

The notation of $^{40}K/K$ is peculiar and possibly confusing. $^{40}K/K$ here means the molar $^{40}K/(^{39}K+^{40}K+^{41}K)$ and is not really a standard notation in isotope geochemistry. It's not obvious to me what a suitable difference would be – my preference would be to simply write $^{40}K/^{39}K$ in the text, and then if necessary, use $^{40}K/K$ in equations (or another symbol indicating fractional ^{40}K). In any case, $^{40}K/K$ needs to be defined quantitatively somewhere in the manuscript.

Other notations are also confusing. The use of lower case "f" and "r" when the uppercase letters are in common use for unrelated quantities in the equations makes this very difficult to read – the sentence on line 80 is a good example of this. It would be more straightforward if Greek letters were substituted.

All quantities used in calculations, decay constants, atomic weights, ages, and other constants should be either listed in the text or tabulated. Almost none of them are listed in the text. They should all be explicitly referenced.

In equation six the symbol for the decay constant is lambda with a subscript lambda. I assume that this is a typo and that it is meant to be lambda subscript new.

Figure 1 is only very slightly modified from Figure 6 in Morgan et al. (2018), which may be a copyright violation. I appreciate that the lead author of that paper is the author of this submission, and that there are only so many ways in which a ranked-data plot can be drafted, and I am not accusing the author of plagiarism or an ethical violation. However, it's clear that the same electronic figure was used in this submission – the fonts, colors, spacing, and all the style characteristics are identical. The "modifications" appear to be just a few extra lines and a couple of arrows. I would urge one of two actions, either the figure be substantially modified so that it no longer resembles that in Morgan et al. (2018), or the publication staff of *Geochronology* confirm that they can legally print this figure via an existing license from the RSC (the publisher of JAAS) or a one-off agreement.

Figure 2: The dots are presumably point estimates of a continuous function, so the curve should be drawn instead of the points, and the plausible range should be bracketed. The point estimates outside of the range were confusing initially before I realized there was an implied curve denoting a continuous function. As mentioned above, this figure would benefit from redrafting as a "change in age vs. absolute age" with an uncertainty band derived from different values of $^{40}K/K$.

Figure 3: The colours are nice, but the figure would be easier to read if it were made wider and had a few labelled contours instead of colours. One has to look back and

forth from the colours to see what the quantities are, and the contours will just be straight lines. They could easily be labelled without cluttering the chart if it were wider, and they could be labelled outside the top and right edges of the figure.