Response to reviewers

Reviewer 1

We would like to thank Anonymous Referee #1 (hereafter referred to as AR1) for their timely and detailed comments.

Overall, we disagree very little with the substance of AR1's review. However, we believe that there is a difference in perspective.

For better or for worse, the geochronological community compiles, calculates, and uses radioisotopic decay constants on its own, independent of the physics community. This is evidenced by the overwhelming use of the K decay constants published in the convention by Steiger and Jager (1977), Min et al. (2000), and to a lesser extent Renne et al. (2010) over any of the compilations favored by the physics community. Indeed, the IUPAC and IUGS have commissioned a committee that publishes critical reviews of decay constants specifically for the chemical and geological community, that largely ignore the physics databases (Villa et al., 2015; Villa et al., 2016; Villa et al., in press; https://doi.org/10.1016/j.gca.2015.05.025; http://dx.doi.org/10.1016/j.gca.2015.10.011; https://doi.org/10.1016/j.gca.2020.06.022).

This manuscript is specifically targeted at geochronologists, who follow the conventions of geochronology, not of the physics literature. We agree with AR1 that our results are not *sensu stricto* new – a major point of the manuscript is that the original personal communication in 1962 is essentially correct. However, geochronologists do not typically follow the physics literature, are likely not to be well-trained in the type of nuclear physics that would recognize as obvious that there must be a complementary ground-state decay mode and are not qualified to judge the approximate magnitude. This manuscript makes this clear *for geochronologists*.

That this is important should be clear from the way that decay constants are used by this community, and the literature from which they draw from. Essentially all $^{40}Ar/^{39}Ar$ and K-Ar geochronology draws on one of the three publications (Beckinsale and Gale 1969; Min et al., 2000; Renne et al., 2010/2011). Among these three, Min et al. and Renne et al. have the strongest underlying analysis and uncertainty structure (Min et al. effectively repeat the analysis embedded in Beckinsale and Gale, but more critically), and Min et al. is currently more popular than Renne et al.

The confusion in the geochronological literature on the ground-state electron capture decay mode can be clearly traced to Min et al. That this is only a single paper does not weaken the argument for our manuscript, it strengthens it.

We strongly believe that there is a good place in the geochronological literature for our analysis; this is also supported by the comments in this regard from Anonymous Referee #2 (hereafter AR2). However, it is clear from the criticisms and comments of AR1 that some of our comments and data presentation may be misleading – we will draft a revised manuscript that takes this feedback into account. These are responded to specifically below.

Response to specific points:

1) *The title is a bit misleading. The paper is dealing with a potential EC branch that contributes with 0.2% to all decays of 40K. Hence, it is not an additional "percent-level production of 40Ar". I also do not agree with "overlooked" since many works consider this potential EC branch (as I will also explain in the following).*

The "percent-level" change is percent of all decays to ^{40}Ar, but we thank AR1 for pointing out that it may be misinterpreted and are happy to change the title of the manuscript. We disagree that it is not "overlooked", inasmuch as it is overlooked by the geochronological community, but we can also clarify this in a revised manuscript.

2) *The motivation of the article is – from my point of view – very weak. It is mainly based on the assertion that this branch is ignored or denied. This is not true. Con- sidering nuclear decay data evaluations, nuclear physicists usually use only the most recent evaluation. Looking to two of the most important evaluation groups (ENSDF and DDEP), we find that an EC branch to the ground state was considered. Hence, the only remaining reference stated is Min et al. (2000). The authors do not mention several other publications which consider this branch. In line 53 they write "Many subsequent workers both in nuclear physics and geochronology have ignored this prediction." but do not provide references.*

(line 69 -71) We state in the manuscript that the ground state branch is included in the ENSDF and DDEP evaluations. The fact that it is included in decay constant evaluations outside of those used by the geochronological community is important because it strengthens the argument that in favor of the presence of a EC ground state decay mode and should be considered (and is why they are discussed in our manuscript). However, simply because these evaluations exist, does not mean that our manuscript is not useful to the geochronolological community: the ENSDF and DDEP evaluations are not used for Ar-Ar or K-Ar dating. The reference to "many subsequent workers" is somewhat confusingly written, and we thank AR1 for highlighting this. We are referring mainly to the many geochronological works that ignore this decay mode, but we do highlight some physics literature on line 82-83, and are also referring to the controversy over the DAMA experiment backgrounds, discussed on line 280. We will reframe this statement to be more clear and refer to specific literature.

3) *"Egelkemeir" (line 70) or Engelkemier (line 73 and Fig. 2, ..) or "Engelkeimer" (Table 1)? Just one example that indicates that the manuscript was not prepared with great care*

We thank the reviewer for bringing this to our attention and the spelling will be corrected.

4) *Several parts in the paper correspond to textbook knowledge in nuclear physics and could be omitted (e.g. large parts in section 4). Moreover, I am wondering whether the theoretical approach presented corresponds still to the state-of-the art. The theory from Bambynek (1977) was a standard for long time, but in the past ~5 years, considerable progress was made by Prof. Mougeot in computation of beta (minus and plus) emission spectra and EC decay probabilities. I think his evaluation can be considered as state of the art. What is new or better in the paper under review? Note that the reference (Mougeot 2019) in Fig. 2 and in its caption should probably read "Mougeot (2018)".*

We are pleased that AR1 reads this section as an explanation of textbook knowledge. The audience for our manuscript is geochronologists, who are typically not versed in nuclear physics, so we have tried to provide a straightforward explanation of the concepts that underpin this decay mode. The feedback from AR2 suggests that this was in fact useful for the geochronologist audience. We did not intend to represent our calculations as state of the art and will clarify this in the revised text by indicating that Mougeot (2018) provides the most robust calculation. Our purpose in providing additional calculations is to demonstrate to an audience of skeptical geochronologists (who may be skeptical of a decay constant that is derived entirely by calculation) that the derived quantity is relatively robust to differences in the way that it is estimated. For this reason we also include the much older Fireman (1949) calculation, and the extremely crude LogFT extrapolation, neither of which would be considered state of the art.

5) *The notations used are sometimes confusing and/or false. For example various expressions are used for the ratio of EC and beta+ decay probabilities. Line 162, the results refers only to K EC.*

We thank AR1 for pointing out these inconsistencies and will fix them in a revised draft.

6) *Is section 3 (in particular its title) justified? The reasoning is based on the assump- tion that a beta plus decay exists. If it exists, I agree that we may also expect an EC to ground state. However, the existence of the beta + with its very low probability in the order of 1E-5 is based on only few experiments. Did the authors consider that detected positrons could also arise from internal pair production as in the decay of 90Y (i.e. from the beta minus side)? In this case, the whole reasoning would collapse.*

We thank AR1 for this observation. We have not considered that the single beta+ experiment might be erroneous, and we have taken the experiments at face value. If this experimental result is incorrect, all the physics literature that we and AR1 cite that includes the ground state decay mode is wrong. It is outside of the scope of this manuscript to redo the experiment, but we will gladly add the caveat in the revised manuscript that this hinges on a single measurement of a low probability decay mode.

7) *Line 204: The authors question the uncertainty stated by Mougeot without provid- ing any argument. At present, Mougeot is one person (perhaps the only) who can accurately calculate beta and EC decay with allowed and unique forbidden transitions.*

(line 215 – 217) We agree with AR1 that this is clumsily worded. The point we were trying to make is that the uncertainty budget for the estimate in Mougeot (2018) is not clearly articulated – it is not clear if the uncertainty presented in that paper is solely propagated from the Q-value as an intermediate precision, or whether it takes into account other sources of uncertainty.

8) Section 5: I cannot agree with the evaluation presented here. First, we must keep in mind that the results are correlated. Hence, a simple statistical consideration is not justified. Moreover, the choice of values that are taken into account appears to be very arbitrary. Most (actually all, except Mougeot) apply outdated models – as the authors do

We take this criticism seriously from AR1. Ultimately, our goal with this manuscript is to provide a simple physics background and argument that will be straightforward to digest by working geochronologists, so that they understand the likely magnitude of a ground state E.C. decay of ^{40}K. In our opinion, it is unlikely that a single estimate – even as cutting edge as possible – is likely to provide a convincing argument to our audience. For this reason, we have provided a range of estimates, using different techniques – yes, some outdated – that all point to a EC_{ground}/β^+ of ~200.

Most of the manuscript is dedicated to harnessing a range of evidence that it is likely that the decay mode exists and has a EC_{ground}/β^+ of approximately 200. Having done this, our next goal was to then communicate the effect this has on the decay rate and branching ratio used in $^{40}Ar/^{39}Ar$ geochronology. For this, it's necessary to use an estimate, or several estimates.

We wanted to provide a reader, who for this journal is likely to be a geochronologist with skepticism that any one estimate will by unbiased or correct with a sense of what the possible range of effects is. The most straightforward way to do this is to group several reasonable estimates together and propagate that variance onto the existing decay rates used by the geochronological community (the values from Min et al.). The result is that the additional decay is negligible for most geochronological inference because it ends up being smaller than other uncertainties. Given that any reasonable EC_{ground}/β^+ produces a negligible effect, we are not concerned that "averaging a number of different calculations" yields a result that was metrologically unsound, as AR1 argues.

It appears that the way we attempted to convey the overall magnitude of the effect of the non-zero EC_{ground}/β^+ gives the wrong impression. We intend on revising the manuscript so that the focus is on the effect of range in calculated EC_{ground}/β^+, and we will highlight and emphasize the Mougeot (2018) calculation as the preferred estimate.

9) *Section 6: Is it justified to use 22Na as cross check? The nature of the decay (al- lowed for the dominant transitions and 2nd forbidden unique for the others) are different than for 40K.*

We agree that 22Na is not a perfect analog, but it is probably the best choice that has a tractable calculation and enough experimental data that the calculation can be reliably verified. In a revised manuscript we will clarify that this is not strictly analogous.

10) *Section 6, Figure 4: There are more data. Why were they excluded? E.g. Applied Radiation and Isotopes, 66, 2008, 865-871 or Mougeot (2018) and Mougeot (2019) (Applied Radiation and Isotopes 154 (2019) 108884).*

(Figure 4) We regret overlooking Nähle et al. (2008), and will include this determination in a revised manuscript, thanks to AR1 for bringing this to our attention. We had not intended to present other calculations for Na22, but on the suggestion of AR1, we would be happy to include them.

11) Line 241: "easy to meaure" I do not fully agree. Also 22Na is challenging, e.g. due to summing effects.

(line 248) In the manuscript, we meant it to be understood as "easier to measure than the ^{40}K ground state decay", rather than imply that the ^{22}Na decay is a straightforward measurement. We thank AR1 for pointing this out, and we will rephrase this section in a revised manuscript.

12) Line 245: x-ray with 511 keV? Perhaps "photon" or "annihilation photon". Also "gamma-ray" would be acceptable.

(line 252) We will correct this statement in the revised manuscript.

13) Line 264: "The orbital electron with the highest probability of capture is from the K-shell; if this electron is captured, it results in the emission of a characteristic x-ray or Auger electron with an energy of 3.2029 keV, the binding energy of the K-shell of 40Ar." No! After K-capture we have the K binding energy available. To eject an X-ray requires the binding energy of another electron in an outer shell. Hence, the x-ray energy is lower than the K binding energy. For Auger processed even 2 additional shells are involved, which also means that x-rays and Auger electron do NOT have the same energy.

(line 273 – 279) We thank AR1 for identifying this confusing statement, and will correct it in a revised manuscript.

14) Line 269: "not tagged correspond to the the electron 270 capture to ground state decay". Really? But then you need 100% detection efficiency for the gamma-rays. "the the"?

(lines 283 - 285) We thank AR1 for identifying this statement and we agree that by this wording is unclear. We will clarify this in a revised manuscript that will state that with a long enough counting period it will be possible to discern those x-rays that are untagged by the 1.46 MeV gamma and those that are tagged effectively observing the electron-capture to ground state decay mode.

15) *Reference "Di Stefano et al.": List of authors is incomplete; Reference can be updated (Journal of Physics: Conference Series)*

We will correct this reference in a revised manuscript.

16) *Line 60: "We describe experiments that could be made to measure this decay mode and also identify observations from nuclear physics experiments that offer evi- dence for its existence" I cannot find a sound description or proposal for such an ex- periment. Section 7 and the supplementary material are very weak. It is not clear how the two EC branches can be distinguished. What about the Auger contributions? If one could clearly identify x-rays as consequence of K EC, one would still need an x-ray emission probability. This is not even mentioned.*

We will correct this statement in a revised manuscript that state we are only carrying out a simple test with the equipment available at SUERC to attempt to detect the ~3keV x-rays associated with both electron capture decay braches of ^{40}K.

17) *In general, the paper contains many formal errors and is not in compliance with ISO standard such as the GUM.*

ISO compliance is typically associated with certification and recertification of processes or products, and it is not clear how the ISO, or a particular ISO standard, is relevant to this manuscript.
Regarding the Guide to Uncertainty in Measurement (GUM; JCGM 100:2008), the estimation of uncertainties follows what that guide refers to as the "law of propagation of uncertainty" described, for example, in section E.3.1 from the GUM. Our manuscript follows some geochemical and geochronological conventions that depart from GUM recommendations, such as notation and reference to "coverage factors" because this is the style of the journal and the community. These "formal errors" are largely an editorial decision, and we are happy to take direction from the editorial staff of *Geochronology* on this matter. We do agree that our uncertainties for this value are misleading in the revised manuscript we will use lower and upper bounds of this value and propagate these through the decay constant determined by Min et al. (2000).

Reviewer 2

We would like to thank Anonymous Referee #2 (hereafter referred to as AR2) for their timely and detailed comments. We are encouraged that they identify as a geochronologist and find this to be a useful contribution to the literature. Overall, we are pleased that AR1 finds no overall fault with our conclusion that on balance, there is good physics-based evidence to support an $EC_{ground}/\beta \sim 200$, and that although AR2 identifies that they do not have the expertise to judge the physics argument, they believe it is a useful contribution to the geochronological literature.

Response to specific comments (numbered as they occur in RC2)

1) *Line 70, Figure 1: In (for example) McDougall and Harrison (1999), the positron decay of 40K to 40Ar is shown as also involving a gamma ray at 1.02 MeV. However, Figure 1 shows the positron decay as direct to the ground state of 40Ar. Please address this discrepancy.*

(line 70) The 1.02 MeV gamma is the sum of the 511 keV annhiliation photons from the interaction of the positron with an electron. This is included in McDougall and Harrison (1999) adapted from Beckinsale and Gale (1969) in which it is not included. The 1.02 MeV will be an observation in any counting experiment however it is not a decay emission and as such we do not include it in Figure 1.

2) *Line ~100: I'll preface this by noting that I'm not a physicist, but why doesn't the energy involved in the gamma ray come into account here? Why is it only the electron capture energy (and not the gamma) that matters? The total energy of the electron capture plus gamma would seem to be sufficient to couple with the positron decay. Also, given the note above (Line 70, Figure 1), is this argument affected by whether the positron decay goes directly to ground state or has an associated gamma?*

(lines 103 – 110) The energy that dictates if positron emission is possible is the Q value. The Q value is the difference between the initial mass state and final mass product. This energy is shared between the outgoing neutrino, atomic excitation of the daughter system, recoil energy, and possibly nuclear excitation of the daughter system. The Q-value therefore includes the excitation of the daughter system. However, positron decay can only compete with the electron capture if the Q value of the electron capture decay itself is greater than the threshold 1022 MeV value requiring the positron decay to go directly to the ground state. We will amend this to provide a clear statement in a revised manuscript.

3) *Line 106: For readers who are not nuclear physicists, a brief explanation of quantum selection rules would make this more readable.*

(lines 121 - 123) Quantum selection rules place formal constraints of the possible transitions of a system from one quantum state to another. In our case it places constraints on the possible set of transitions from the parent ^{40}K state to the daughter ^{40}Ar. We will include this definition in the revised manuscript.

4) *Figure 2 caption: Perhaps note that uncertainties were either not estimated or are smaller than the symbols? This is stated in the text but would be ideal to have in the caption as well.*

(Figure 2 caption) We will indicate in the caption that the uncertainties are either unknown or too small to plot.

5) *Line 287 (and throughout): The use of 'flux monitor' is a common error – should be 'fluence monitor', as they are measuring the total neutron fluence (flux over time) af- fecting samples over the entire irradiation, rather than monitoring the neutron flux at one specific time.*

(Lines 300, 320, 322, 333) We will correct flux monitor to fluence monitor.

6) *Line 303: Based on Figure 5, I calculate a different percent decrease for K-Ar ages at 1 Ga (2.5%, for ca. 25 Ma at 1 Ga, rather 1.3%). The value 0.7% at 4.5 Ga seems accurate, and the 1.6% at 1 Ma is not identifiable (due to scaling of graph) in the figure. It would be helpful to have an expanded Figure 5, with multiple scales (or just expand this scale down to 1 Ma) to highlight different parts of the geologic timescale. It would also be helpful to show results in relative values as well as absolute values. Finally, the K-Ar line seems to have structure (e.g. around 10ˆ8 a) that should be explained.*

(line 319 – 340) For a $^{40}Ar/^{40}K = 0.08$, and using the decay constants in our Table 1 (λ_{EC*} = 0.580e-10 and λ_{total} = 5.463e-10 for Min et al; and λ_{EC*} = 0.590e-10 and λ_{total} = 5.473e-10;), we used the K-Ar equation:

$$time = \frac{1}{\lambda_{total}} * \ln\left(1 + \frac{\lambda_{total}}{\lambda_{Ar}}\ or\ \frac{EC^{*40}Ar}{^{40}K}\right)$$

This yields dates of 1028.05 Ma and 1014.24 Ma for the Min et al. and our revised decay constants, respectively. This is a difference of 13.81 Ma, or about 1.3 %. We have reproduced this calculation and believe that our original calculation is correct, though we welcome any correction from AR2 if we have misunderstood.

In a revised manuscript, we will provide a figure that provides more detail. The small kink at 100 Ma is an Illustrator artifact and will be smoothed in a revised manuscript.

7) *Line 306: I'm struggling to understand the use of a fluence monitor at 23.2 Ma. I realize this is (may be?) a theoretical monitor, but it's in a paragraph with clear reference to Fish Canyon sanidine and I've spent some time wondering if '23.2' was a typo for '28.2 Ma'. Actually, I'm still not sure – is this a typo? If not, perhaps just note that it's a theoretical monitor of arbitrarily chosen age (if that's indeed what it is), to prevent others from wondering the same.*

(line 322- 323) we will change the date to 28.2 Ma.

Technical Corrections:

1) *Line 97: "They are linked because both processes have the same initial and final nu- clear states." It's not clear what 'they' refers to – likely electron capture and positron, but perhaps beta?*

(Line 99) "They" refers to EC and positron, and will be clarified in the revised text.

2) *Line 124: The symbol is missing from the pdf for type of emission*

(line 137) The missing quantity is a beta, and we will ensure this is typeset correctly in a revised text.

3) *Line 148: Is Emax defined somewhere?*

(line 164 - 165) Unfortunately we neglected to define E_max, but will do so in a revised text.

Relevant changes to manuscript

(1) The title has been modified to stress the implications of this decay mode for K-Ar dating

(2) Figure 2 has been changed to remove the preferred value.

(3) Figure 4 has been amended to include the Nähle et al. (2008) reference as suggested by reviewer 1.

(4) Table 1 has been changed to include modified decay constants using a lower and upper bound value for the electron capture to positron ratio of the ground state decay.

(5) Figure 5 has been changed to a 2 panel figure with the left panel showing both change in age using the $^{40}Ar/^{39}Ar$ equation with independently calibrated standards using both the lower bound and upper bound values of the EC_{groudn}/β^{+} ratio. The right panel shows the change in age using the K-Ar equation using both the lower and upper bound values. Both panels now include inset figures that show the fractional differences in age by the inclusion of both the upper and lower bound EC/β^{+} value.

Production of ^{40}Ar by an overlooked mode of ^{40}K decay with implications for K-Ar geochronology

Jack Carter[1], Ryan B. Ickert[1,2], Darren F. Mark[1,3], Marissa M. Tremblay[2], Alan J. Cresswell[1], David C.W. Sanderson[1]

[1]SUERC, Rankine Avenue, Scottish Enterprise Technology Park, East Kilbride, G75 0QF
[2]Department of Earth, Atmospheric, and Planetary Sciences, Purdue University, West Lafayette, IN 47901
[3] University of St Andrews, College Gate, St Andrews, KY16 9AJ, Fife, Scotland, UK

Correspondence to: J. Carter (j.carter.1@research.gla.ac.uk)

Abstract. The decay of ^{40}K to the stable isotopes ^{40}Ca and ^{40}Ar is used as a measure of time for both the K-Ca and K-Ar geochronometers, the latter of which is most generally utilized by the variant ^{40}Ar/^{39}Ar system. The increasing precision of geochronology has forced practitioners to deal with the systematic uncertainties rooted in all radioisotope dating methods. A major component of these systematic uncertainties for the K-Ar and ^{40}Ar/^{39}Ar techniques is imprecisely determined decay constants and an incomplete knowledge of the decay scheme of ^{40}K. Recent geochronology studies question whether ^{40}K can decay to ^{40}Ar via an electron capture directly to ground state (EC_{ground}), citing the lack of experimental verification as reasoning for its omission. In this study, we (1) provide a theoretical argument in favour of the presence of this decay mode, and (2) evaluate the magnitude of this decay mode by calculating the electron capture to positron ratio (EC_{ground}/β^+) and comparing calculated ratios to previously published calculations, which yield EC_{ground}/β^+ between 150-212. We provide support for this calculation through comparison of the experimentally verified EC_{ground}/β^+ ratio of ^{22}Na with our calculation using the theory of β decay. When combined with measured values of β^+ and β^- decay rates, the best estimate for the calculated EC_{ground}/β^+ for ^{40}K yields a partial decay constant for ^{40}K direct to ground state ^{40}Ar of $11.6 \pm 1.5 \times 10^{-13}$ a^{-1} (2σ). We calculate a partial decay constant of ^{40}K to ^{40}Ar of $0.592 \pm 0.014 \times 10^{-10}$ a^{-1}, total decay constant of $5.475 \pm 0.107 \times 10^{-10}$ a^{-1} (2σ), and conclude that although omission of this decay mode can be significant for K-Ar dating, it is minor for ^{40}Ar/^{39}Ar geochronology and is therefore unlikely to have significantly biased published measurements.

1. Introduction

^{40}K is a naturally occurring radioisotope of K with atomic abundance of 0.0117% (Garner et al., 1975). ^{40}K undergoes a branched decay to ^{40}Ar and ^{40}Ca with a total half-life of ca. 1.3 Ga, and is the basis of the K-Ca and the K-Ar geochronometers (Aldrich and Nier, 1948; Wasserburg and Hayden, 1955; Marshall and DePaolo, 1982). The K-Ar system is most often exploited using the variant $^{40}Ar/^{39}Ar$ method, wherein some of the ^{39}K in the sample is transmuted to ^{39}Ar by irradiation with fast neutrons, thereby allowing both the parent and the daughter nuclides to be measured as isotopes of Ar (Merrihue and Turner, 1966). The latter is widely used to date geological events that span Earth history, from volcanic eruptions recorded in historical texts (e.g., Preece et al., 2018; Renne et al., 1997), to the earliest events in the solar system (e.g., Renne, 2000).

Advances in analytical precision have forced practitioners in geochronology to address systematic uncertainties that are inherent in all radioisotope dating methods, such as uncertainties in the measurement apparatus, prior assumptions made by the observer, or interference from environmental factors. For the K-Ar system, these uncertainties also include those that arise from imprecisely known decay rates of ^{40}K. In the geological literature, there have been two influential reviews of measurements of the ^{40}K decay rate. Beckinsale and Gale (1969) provided the first comprehensive review of measured and predicted decay rates, which became the basis of the convention adopted by Steiger and Jäger (1977) used by the geochronological community for the next 20 years. Subsequently, Min et al. (2000) provided a more lengthy, critical review of available specific activity data determined by direct measurements of decay, and updated the derived decay rates for newer physical constants. More recently, the ^{40}K decay parameters were estimated by Renne et al. (2010a,b), and although direct measurements of the ^{40}K decay were incorporated into the estimate, it was heavily weighted to an intercomparison with ^{238}U decay. The decay rate determined by Renne et al. (2010, 2011), and the Min et al. (2000) decay rates are the most frequently used in $^{40}Ar/^{39}Ar$ geochronology. These evaluations, along with those from the nuclear physics community, have been summarized recently by Cresswell et al. (2018, 2019).

Despite decades of work and longstanding interest in ^{40}K decay, there remains uncertainty over the nature of the decay scheme. There is consensus that most ^{40}K decays by β^- to ^{40}Ca or by electron capture to ^{40}Ar via an excited state, and that a small amount (~ 0.001%) of ^{40}K decays to ^{40}Ar via β^+. The early but influential review of ^{40}K decay by Beckinsale and Gale (1969) included these decay modes, and also included a prediction of a second electron capture decay directly to the ground state of ^{40}Ar that would add an additional ~2% to the rate of decay from ^{40}K to ^{40}Ar. Many workers in geochronology (e.g., those who use the Min et al., 2000 decay constants) have ignored this prediction, and some nuclear physics tabulations do not clearly include it (Endt 1990, Audi et al. 2003). The influential review by Min et al. (2000) described this decay mode as "unverified" and having a "questionable" existence.

However, the putative electron capture to ground state decay mode decay constant is of the same order of magnitude as the uncertainties in the decay rate of ^{40}K to ^{40}Ar, and therefore may be a non-negligible and potentially important part of the geochronological system. Here, we describe the theoretical basis of this predicted decay mode and demonstrate the robust nature of the prediction via an analogous calculation of ^{22}Na decay. We describe experiments that could be made to measure this decay mode and also identify observations from nuclear physics experiments that offer evidence for its existence. We conclude that the evidence for this decay mode is strong, and despite the large uncertainty, should be considered in evaluations of the ^{40}K decay rate.

2. Historical Overview

At present, ^{40}K has three experimentally-verified decay modes (Figure 1):

1) β^- decay to ^{40}Ca. This mode can be verified by direct measurement of the β^- emission.
2) Electron capture to an excited isomer of ^{40}Ar, followed by decay to the ground state of ^{40}Ar accompanied by emission of a 1.46 MeV γ-ray. Hereafter we denote this decay mode as EC*. This mode can be verified by direct measurement of the γ emission.
3) β^+ decay from the ground state of ^{40}K to the ground state of ^{40}Ar (Engelkemeir et al., 1962). This is a very small component of the total decay rate and has been verified by direct measurement of the β^+ emission.

In their paper reporting the measurement of β^+/β^-, Engelkemeir et al. (1962), through a private correspondence with Brosi and Kettle, proposed that an electron capture mode that goes directly to ground state ^{40}Ar also exists, with an electron capture to positron ratio of 155. This decay mode is hereafter denoted EC_{ground}. This decay mode has not been experimentally detected, in part because the measurement is much more difficult to make than the others. If it exists, it would contribute about 0.2% to the total decay rate of ^{40}K, or about 2% to the ^{40}Ar branch.

The EC_{ground} decay mode was included in the review by Beckinsale and Gale (1969) and then subsequently in Steiger and Jäger (1977). This decay mode is also included in the widely-used ENSDF and DDEP evaluations (Chen, 2017 and Mougeot & Helmer, 2009 respectively). However, evaluations by Endt and Van der Leun (1973, 1978), Endt (1990), Audi et al., (2003) do not explicitly include this decay mode, with Audi et.al. (2003) giving a transition intensity which is the combined EC* and β^+ intensities. Min et al., (2000) have questioned its validity because there is no experimental verification, and therefore do not include EC_{ground} in their estimates.

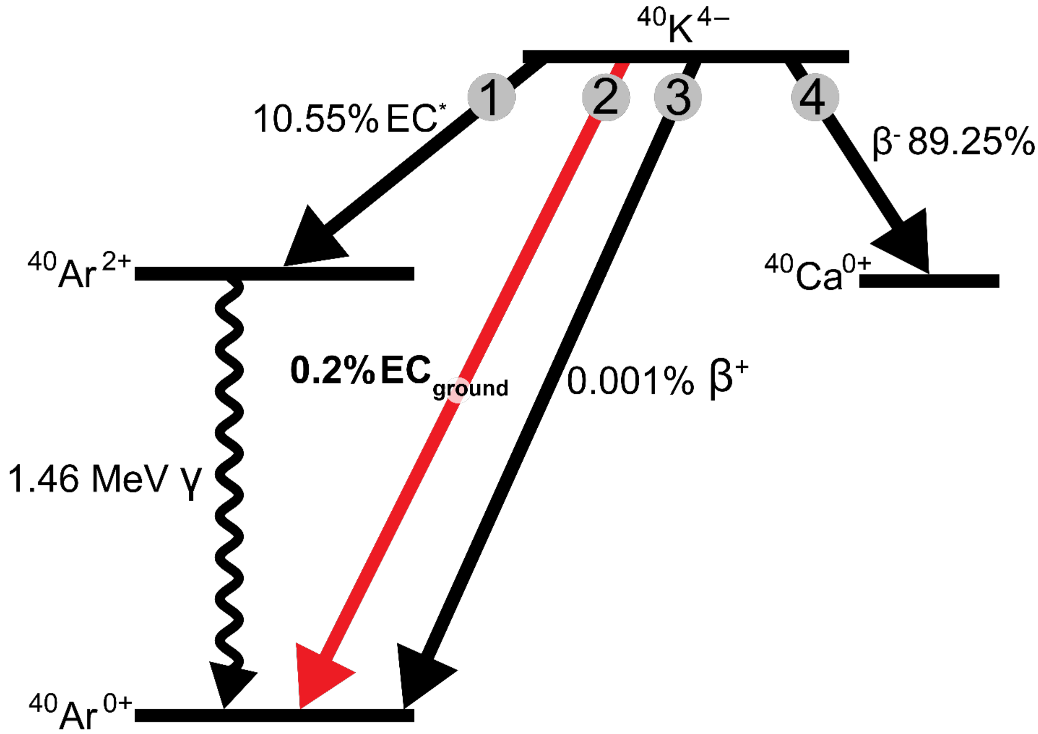

Figure 1: Decay scheme of ^{40}K after McDougall and Harrison (1999) and Leutz et al., (1965), where 1 is the electron capture branch to the excited state of ^{40}Ar with y-ray emission (EC*), 2 is the electron capture direct to the ground state of ^{40}Ar (EC_{ground}), 3 is the positron decay to ground state of ^{40}Ar, and 4 is the *β* decay to the ground state of ^{40}Ca. The disputed decay mode, EC_{ground}, is highlighted in red.

3. Why there must be an EC_{ground} decay mode

In nuclides that are too proton-rich and therefore radioactive, protons decay to correct this imbalance via two mechanisms. Either, (1) the nucleus undergoes electron capture wherein an orbital electron is captured by the nucleus, or (2) the nucleus emits a positron (β^+). Both processes are types of β decay and result in the transformation of a proton to a neutron to conserve charge, and they both also emit a neutrino in order to conserve lepton number and energy. These two processes are typically paired: coupled electron capture-β^+ is the second most abundant decay type on the chart of the nuclides, after β^- decay (Audi et al., 2003). The electron capture (EC) and positron (β^+) decay modes are linked because both processes have the same initial and final nuclear states.

β^+ decay is always accompanied by EC, but the converse is not always true (Bambynek et al., 1977). This is because β^+ decay, unlike EC, requires a minimum amount of energy (~1022 keV, equivalent to the combined rest masses of both a positron and an electron) in order to produce the emitted positron and an electron (the latter to satisfy charge conservation). The energy between initial and final states is the Q value, which is a function of the difference between the initial and final masses. This energy is shared between the outgoing neutrino, atomic excitation of the daughter system, recoil energy, and nuclear excitation of the daughter system. The energy which dictates if positron emission is possible is denoted Q_{EC}. In the decay of ^{40}K, the EC* branch has an energy difference (Q_{EC}) between the initial and excited isomer state of only 44 keV. In contrast, the energy difference between ^{40}K and the ground state of ^{40}Ar, is 1504.4 keV (Wang et al., 2017), an energy greater than the combined rest masses of the positron and electron. Therefore, the EC* branch, with energy difference of only 44 keV, *cannot* be the complement to the β^+ decay and the EC_{ground} *must* exist to provide the β^+ complement. The experimental observation of the β^+ decay mode comes from a single measurement by Engelkemeir et al. (1962). We rely on this measurement to make our argument for the existence the EC_{ground} . It is possible that the positrons observed arise from the pair production of the ~1460 keV gamma; Engelkemier et al. (1962) discuss this possibility in their experiment, calculating this as 55-60% of the total positron detection rate. However, positrons produced by this mode of pair production would be monoenergetic at 440 keV, whereas the observed positron energy spectra exceed this value, with a maximum of 491 keV. A reasonable fit is also observed between the measured β^+ energy spectrum and the theoretical 3rd forbidden unique energy spectrum, supporting the argument that these β^+ are from a decay mode rather than arising from pair production.

4. Theory and Calculation of EC_{ground}/β^+

In the decay of ^{40}K, the nuclide can reach a more stable state (^{40}Ca or ^{40}Ar) only by violating quantum selection rules. Quantum selection rules place formal constraints of the possible transitions of a system from one quantum state to another. In this case it places constraints on the possible set of transitions from the parent ^{40}K state to the daughter ^{40}Ar. Decays which violate these selection rules undergo slow, so-called 'forbidden' unique transitions, which give ^{40}K its long ~1.3 Ga half-life. The ^{40}K decay scheme itself is unusual because the coupled EC_{ground}-β^+ and β^- branches are the only third order unique forbidden transitions known in nature. All ^{40}K decays undergo a parity reversal (where parity reversal is the change of sign in one of the spatial coordinates *(x, y, z)*) between the initial parent state and final daughter state. Therefore, we can define the selection rules as:

$$'|\Delta J - 1|^{st} order\ unique\ forbidden\ decay\,'$$

where $\Delta J = J_i - J_f$, is the change in spin from initial to final state following Krane and Halliday (1987). We can characterize each decay mode of ^{40}K by its degree of forbiddenness from the above selection rule. The EC* mode undergoes a spin change of $\Delta J = 4 - 2 = 2$ and is classified as a first order unique forbidden decay. The three other decay modes of ^{40}K, including EC_{ground}, all undergo a spin change of $\Delta J = 4 - 0 = 4$ and are classified as 3rd order unique forbidden decays.

The EC process occurs because the atomic electrons have a finite probability to be in the nucleus with the likelihood of being captured highest for those closest to the nucleus. A theoretical description of β emission was first given by Fermi (1934), while the possibility of electron capture which was first recognized by Yukawa and Sakata (1935) and later developed by Bethe and Bacher (1936). Here we use Fermi theory of β^- decay to calculate the EC_{ground}/β^+ in the decay of ^{40}K.

We can use the ratio of orbital electron capture and positron emission to infer the existence of EC_{ground}. The ratio *br* is defined as:

$$br = \frac{\lambda_{ec}}{\lambda_{\beta+}}, \quad (1)$$

Where λ_{ec} and $\lambda_{\beta+}$ are the probability per unit time of electron capture or β^+ emission. In electron capture, orbital electrons can be captured from any orbital shell of the atom. The EC/β^+ is therefore the summation of the individual capture ratios from each shell. Following Bambynek et al. (1977), the total electron capture-to-positron ratio is:

$$\frac{\lambda_x}{\lambda_{\beta+}} = \frac{\sum_x n_x C_x f_x}{f_{\beta^+} C(W)}, \quad (2)$$

where x is the shell, n_x is the relative occupation number, C_x contains the dependence of electron capture rates on nuclear structure giving the forbiddenness classification, similar to the shape factor in β decay (Emery, 1975), f_x is the integrated fermi function in β decay, $f_{\beta+}$ is the integrated positron spectrum, and *C(W)* is the theoretical shape factor for allowed or forbidden transitions. A review of shape factors for ^{40}K transitions is provided by Cresswell et al. (2018, 2019). We initially simplify this equation to only consider the innermost K shell, the shell containing the electron with the highest probability to be captured by the nucleus:

$$\frac{\lambda_k}{\lambda_{\beta+}} = \frac{n_k C_k f_k}{f_{\beta^+} C(W)}, \quad (3)$$

where λ_K is the probability of K-shell capture. For this capture, f_K is defined as:

$$f_k = \frac{\pi}{2} q_k^2 \beta_k^2 B^k, \quad (4)$$

where q_K is the momentum of the neutrino particle, β_K is the Coulomb amplitude of the wave function, and B_K is the term for overlap and exchange corrections. Similarly, $f_{\beta+}$ is defined as:

$$f_{\beta^+} = \int_1^{W_0} F(-Z, W) W p (W_0 - W)^2 dW, \quad (5)$$

$$W = 1 + \frac{E_T}{m_e}, \quad (6)$$

$$W_0 = 1 + \frac{E_{max}}{m_e}, \quad (7)$$

$$p = \sqrt{W^2 - 1}, \quad (8)$$

where W is the total energy of the positron given by its kinetic energy E_T and rest mass m_e, defined above, and the momentum of the positron is given by p (eq. 8), W_0 is the total normalized energy defined above, E_{MAX} is the upper limit of the positron energy (equal to the Q value of the decay), and F(-Z,W) is the Fermi function. We follow Bambynek et al., (1977) in the formula for $\frac{C_K}{C(W)}$ which is given by:

$$\frac{C_K}{C(W)} = [(2L-1)!]^{-1} q_K^{2(L-1)} \left\{ \sum_{n=1}^{L} \lambda_n p^{2(n-1)} ((2n-1)!\,[2(L-n)+1]!)^{-1} \right\}^{-1}, \quad (9)$$

where L = ΔJ, and L = 1 for ΔJ = 0. The parameter λ_n cannot be calculated in a straightforward manner and therefore we follow a typical assumption that $\lambda_n = 1$ (Huber, 2011). This reduces the above expression to:

$$\frac{C_K}{C(W)} = \frac{q_K^6}{p^6 + q^6 + 7p^2 q^2 (p^2 + q^2)}, \quad (10)$$

In a given decay, the change in charge from the initial to final state can lead to an imperfect overlap of the wavefunctions of these states. Furthermore, given the indistinguishability of electrons, there is the possibility of an exchange effect wherein an electron does not necessarily come from the orbital where the vacancy appears. For instance, it is possible that a vacancy may appear in the K-shell but the captured electron from an outer shell is then subsequently filled by the inner shell electron (Bahcall, 1962; Bambynek et al., 1977). We follow Bahcall (1962) in implementing corrections for these effects, resulting in $B_K = 0.979$. Then using nuclear data given in Bambynek et al. (1977) we estimate an EC_{ground}/β^+ of 148.

We first note that this value is in approximate concordance with the private correspondence value in Engelkemeir et al. (1962). However, this is only the capture ratio from the K-shell so we extend our model to a total electron capture ratio from all orbitals following Bosch et al. (1977). The total electron-capture-to-positron ratio, an extension of Eq.1, is given by:

$$\frac{EC}{\beta^+} = \frac{K}{\beta^+}\left(1 + \frac{L}{K} + \frac{M}{L}\frac{L}{K} + \cdots\right), \quad (11)$$

We can simplify this equation by neglecting shells that make a negligible contribution. In ^{40}K the probability of capture is dominated by the two inner shells K and L1, with approximate probability of ca. ~90% and ~10% with a negligible contribution from the shells further out. We can therefore omit all shell captures except K and L1 to arrive at the total EC_{ground}/β^+ ratio:

$$\frac{EC}{\beta^+} = \frac{K}{\beta^+}\left(1 + \frac{L_1}{K}\right), \quad (12)$$

The ratio of each shell capture can be solved with the following equation:

$$\frac{x}{K} = \frac{\beta_x^2 (W_0 - W_x)^2 B_x}{\beta_K^2 (W_0 - W_x)^2 B_K}, \quad (13)$$

where x = L1 and the other symbols have the same definition as above. Using this equation we calculate a total EC_{ground}/β^+ of 164.

To further estimate the magnitude of the electron capture decay mode, we can perform another calculation of EC_{ground}/β^+ following Fireman (1949). This simplified form of the calculating EC_{ground}/β^+ is dependent only on the Q value (the difference between the initial and final state energies). This is given by:

$$\frac{\lambda_{ec}}{\lambda_{\beta^+}} = \frac{(\eta+2)^8}{0.450\eta^{6.5}} \frac{1}{0.0676 + 1.25\eta + 8.48\eta^2 + 12.5\eta^3 + 1.74\eta^4 + 0.079\eta^6}, \qquad (14)$$

where $\eta = \frac{Q}{m_e} - 2$. We calculate an EC_{ground}/β^+ of 272 using this method and the updated Q-value of Wang et al. (2017). We note that despite discrepancies in these values for each method of evaluation, they are of the same order of magnitude. The differences in the values in these evaluations highlight the need for experimental measurement of EC_{ground}/β^+.

5. Comparison with other evaluations

Other theoretical evaluations of EC_{ground}/β^+ for ^{40}K exist in the literature (Figure 2). Pradler et al. (2013) and Mougeot (2018) report ratios of 150 and 212 ± 0.15, respectively (uncertainties are reported where they have been estimated). These workers use broadly similar methods as us. Mougeot (2018) uses higher order corrections for both exchange and overlap and accounts for the dependence of λ_K, that we set equal to 1 in Eq.9, on the energy of the decay. Pradler et al. (2013) use the Fermi method and data from Bambynek et al. (1977) but only perform the calculation for K-shell electrons, resulting in a slightly different calculated value than we report. Notably, all estimated values are of the same order of magnitude, similar to the ratio 155 reported in Engelkemeir et al. (1962), and our calculated value of 164. Currently, the most commonly-used EC_{ground}/β^+ value is calculated via the LogFT program, a program used in nuclear data evaluations (ENSDF Collaboration, LOGFT). However, the program is capable of only calculating first and second unique forbidden decay ratios, so the EC_{ground}/β^+ value from LogFT of 200 ± 100 is an extrapolation, with the assumption that the increase in the ratio from second to third order is by the same factor as the increase from first to second order. Finally, Chen (2017) evaluates the ^{40}K decay data and reports a EC_{ground}/β^+ value of 45.2 ± 1.4 without elaboration.

The variability between the modern estimates are driven primarily by choices when making the approximations necessary for these calculations to be tractable. Uncertainties on individual estimates which could be derived by propagating the uncertainties in the underlying experimental data are small and where uncertainties are estimated, are generally not explicated.

The value calculated by Mougeot (2018) of 212 ± 0.15 is currently the best estimate of the ^{40}K EC_{ground}/β^+. It is slightly higher than two other recent estimates, our value of 164 or that of Pradler et al. (2013) of 150. Given a broad consensus in calculated EC_{ground}/β^+ over several decades and via a variety of methods, it appears highly likely that it falls in the range 150-212 (Fig. 2).

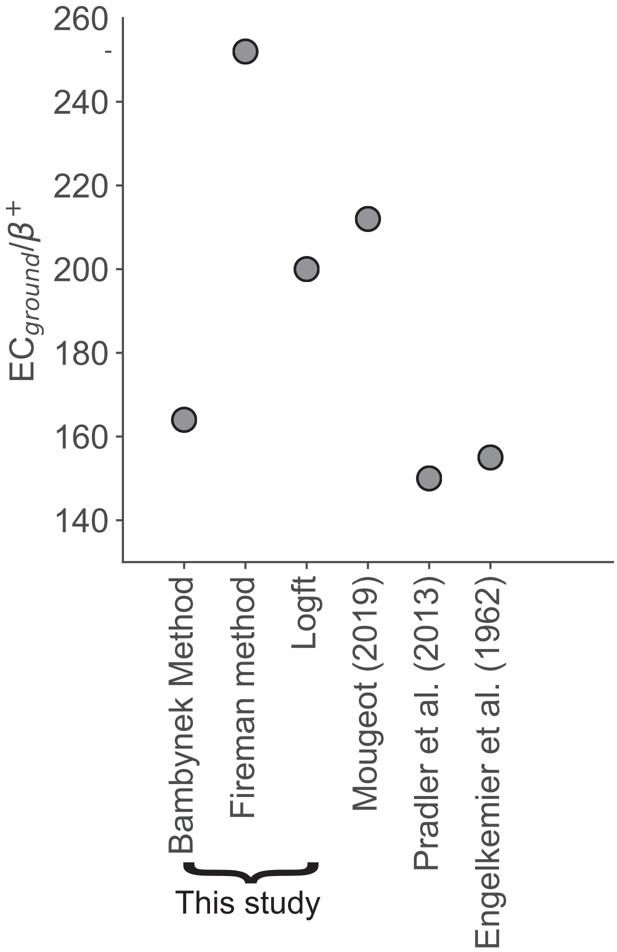

Figure 2: Comparison of theoretically calculated EC_{ground}/β^+ of ^{40}K in this study using three methods; (1) Bambynek Method (Bambynek et al. (1977)), (2) Fireman method (Fireman, 1969), and (3) Logft (LogFT, 2001). The value of Chen (2017) is not included in the figure as it is an extreme outlier and the authors do not explain the method they use to reach this value. Our calculated ratios are compared to previous evaluations in the literature (Engelkemeir et al. (1962); Pradler et al. (2013); Mougeot, 2018). Uncertainties in these values are either intractable or in the case of Mougeot (2018) too small to plot.. Note the consistency in the estimated ratio from all of the methods.

6. Comparison with ^{22}Na

To test the validity of our ^{40}K EC_{ground}/β^+ estimate, we use the same calculations to estimate the experimentally-constrained $(EC/\beta^+)^*$ value for ^{22}Na decay. ^{22}Na is radionuclide with a half-life of ~2.6 years, it occurs in nature as a low-abundance cosmogenic nuclide produced by spallation of ^{40}Ar and is also produced synthetically by proton irradiation for use in positron emission tomography. Like ^{40}K, it decays by electron capture and positron emission. The main EC-β^+ pair for ^{22}Na decays initially to the excited state of ^{22}Ne, followed by a 1.27 MeV γ emission (Figure 3; Bé et al., 2006). This pair has a $(EC/\beta^+)^*$ of approximately 0.1 and accounts for >99.9% of the total decay. A second EC-β^+ pair decays directly to the ground state of ^{22}Na with an $(EC/\beta^+)_{ground}$ of ~ 0.02, but is a minor component. Here, we calculate the $(EC/\beta^+)^*$ for the main branch. Unlike ^{40}K, the dominant decay of ^{22}Na is the β^+ decay mode. This is due to the greater difference in energy between the initial and final states, as positron decay will have a greater possibility of occurring in decays with a greater mass differences between initial and final states (Emery, 1975). ^{22}Na is not a perfect analogue, however it is probably the best choice that has both a tractable theoretical calculation and a wealth of experimental data which can be used readily for verification.

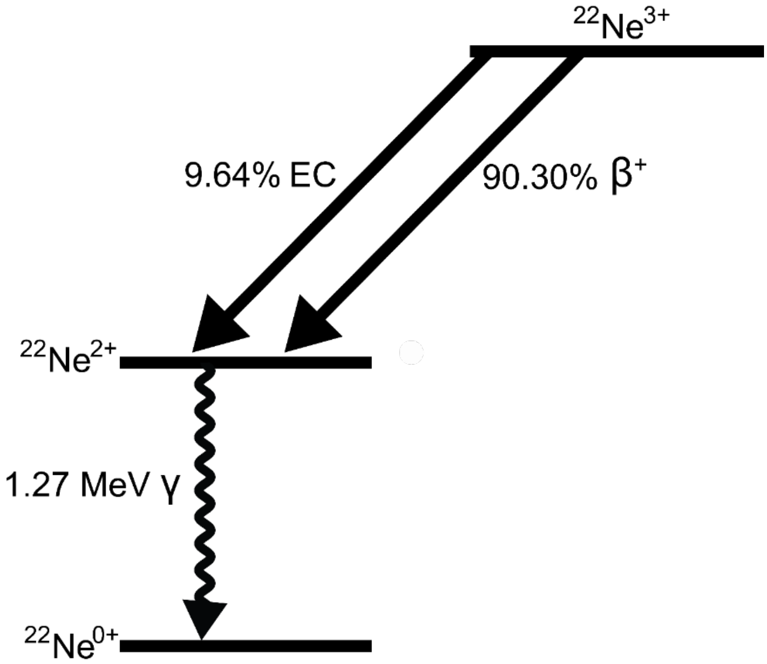

Figure 3: Decay scheme of ^{22}Na after Bé et al. (2006) and Leutz et al. (1965). An additional EC and β^+ decay pair that corresponds to approximately 0.056% of the total decay of ^{22}Na has been omitted for clarity.

Unlike ^{40}K, there are numerous measurements of the electron capture to positron ratio for decay to the excited state of ^{22}Ne (Figure 4; Kreger, 1954; Vatai et al., 1968; Williams, 1964; McCann and Smith, 1969; Mac Mahon and Baerg, 1976; Bosch et al., 1977; Baerg, 1983; Schmidt-Ott et al., 1984; Sykora and Povinec, 1986; Kunze et al., 1990). Measurement of $(EC/\beta^+)^*$ for ^{22}Na is accomplished by measurement of both of the gammas (which come from both the EC* and the β^{+*}) and the x-rays (which only come from the EC branch). Relative to the ^{40}K EC_{ground}/β^+ , the ^{22}Na $(EC/\beta^+)^*$ is a more straightforward measurement because of the higher activity (meaning higher count rate) and the higher energy of the x-ray emitted from the Auger electron, which an electron from the same atom that is emitted as a vacancy of an inner shell is filled. In a decay to the excited state of ^{22}Ne, the de-excitation 1.28 MeV γ will be associated with both electron capture and positron decay. However, those measured 1.28 MeV γ that are not accompanied by two 0.511 MeV annihilation photons can be used to distinguish between both processes. We use the experimental measurements to verify our calculations described above for ^{40}K.

Following a similar calculation using the Fermi method, our preferred method, to that used for our proposed estimate of the ^{40}K EC_{ground}/β^+, we estimate an $(EC/\beta^+)^*$ of approximately 0.11. This is within the range of measured values of 0.105-0.115 (Fig. 4), suggesting that our calculation strategy of the the ^{40}K EC_{ground}/β^+ is accurate, and lends further confidence to the existence of the current unmeasured ^{40}K electron capture to ground state decay.

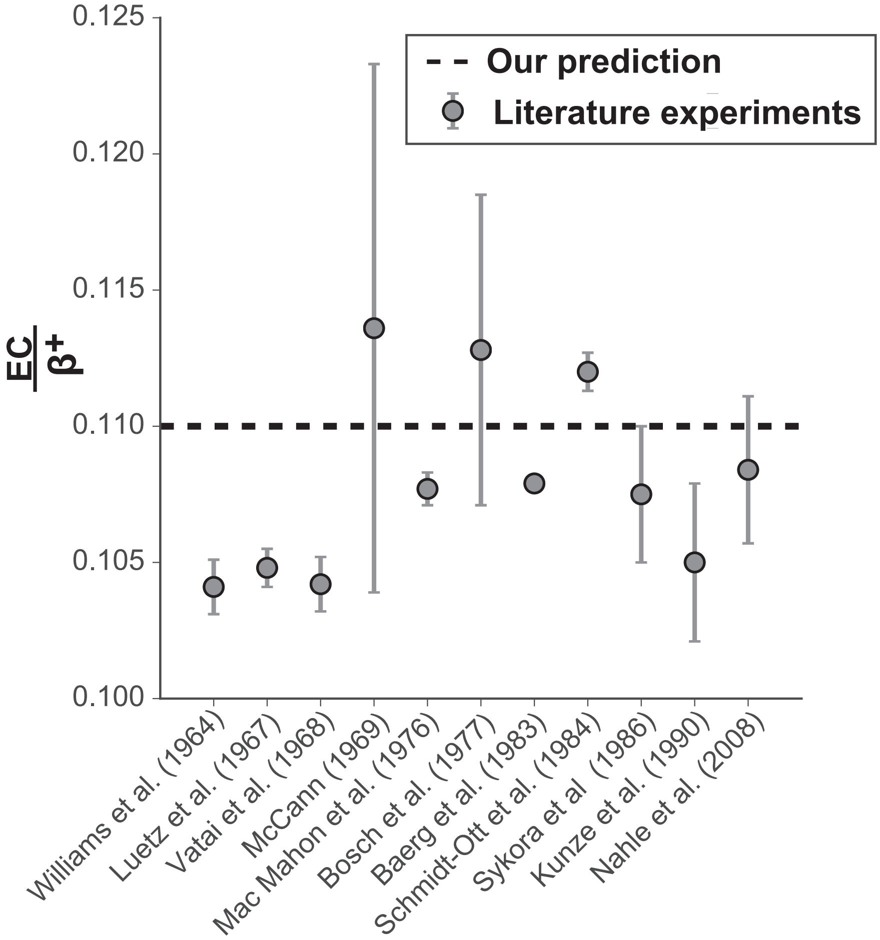

Figure 4: Comparison of experimentally measured $(EC/\beta^+)^*$ ratios of ^{22}Na (grey circles) adapted from Kunze et al. (1990) with our calculated value (black dashed line). Note the concordance of the theoretical and experimental determinations. The uncertainty in the Baerg et al. (1983) determination is smaller than the symbol.

7. Experimental verification of EC_{ground} decay mode

In both β^- and β^+ decay, an electron or positron is emitted which allows for direct detection and verification of the decay process. In contrast, electron capture cannot be detected directly. Methods to experimentally verify electron capture rely on indirect processes associated with the rearrangement of the atom following the capture of the orbital electron. Once the electron is captured the atom will rearrange itself to fill the vacancy, resulting in the emission of a characteristic x-ray or Auger electron with an energy defined by the binding energy of the shell vacancy of the daughter nucleus.

In the case of ^{40}K, verification of the EC_{ground} decay can be achieved by measuring the characteristic x-rays (Di Stefano et al., 2017). The orbital electron with the highest probability of capture is from the K-shell; if this electron is captured, the resulting vacancy in the K-shell may be filled by an electron from any of the other shells (e.g., L, M, …), and a characteristic x-ray is emitted with an energy dependent on the particular shell that fills the vacancy. It is not necessary, however, that all K-capture processes result in the emission of an x-ray. By the Auger effect, a radiationless transfer may occur wherein the K-shell vacancy is replaced by two vacancies in the next outer shell, L, or one in the next two shells; L and M. The energies of the Auger electrons emitted in these transitions depend upon the ^{40}Ar product resulting from K-capture. Both electron capture decays to the ground and excited state of ^{40}Ar ($^{40}Ar^{2+}$) result in the same electron configuration and x-ray emissions. Di Stefano et al. (2017) suggested tagging x-rays with the de-excitation γ associated with electron capture to $^{40}Ar^{2+}$, which has a lifetime on the order of ~ 10^{-12}s (Di Stefano et al., 2017). Measuring these tagged x-rays experimentally will be challenging since it requires identifying a low probability decay mode with x-ray signals present against a high background from the $^{40}Ar^{2+}$ state. Further, as illustrated in Di Stefano et al. (2020), it is expected that 50 EC* decays occur for every 1 EC_{ground} decay; therefore a detector efficiency of ≥ 98% is required to make sure that there is fewer than one mis-tagged EC* decay for each true EC_{ground} decay. The experiment therefore requires an x-ray spectrometer able to resolve the Ar-K x-ray from other x-rays in the background, and accurately account for the x-ray–γ-ray coincidence efficiency (≥ 98%) to quantify x-ray emission rates in excess of those from the $^{40}Ar^{2+}$ state. Given the complexity involved in this experiment, a pilot study was conducted at SUERC to measure characteristic x-rays from a KCl source. The experiment was not successful because the detector was not able to resolve the Ar-K x-ray sufficiently but demonstrates the potential of this method to detect the x-rays, given a sufficiently high-resolution detector. Full details are provided in the supplementary material.

Ongoing attempts are being made to verify this decay mode by careful detection of the characteristic x-rays by the KDK experiment (Di Stefano et al., 2017; Stukel, 2018). Experimental verification has implications for (1) rare event physics, as it is a vital component in constraining the irreducible background and verifying results in the DArk MAtter (DAMA) experiment (Pradler et al., 2013), (2) the theory of β- decay (Fermi, 1934) as it is the only 3rd order unique forbidden electron capture decay known (Audi et al., 2003), and (3) K-Ar and $^{40}Ar/^{39}Ar$ geochronology, for which it is currently overlooked due to lack of experiment evidence. We further expand on the implications for geochronology below.

8. Relevance for geochronology

Geochronology with the K-Ar system requires either both the branching ratio and the total decay constant, or in the case of an $^{40}Ar/^{39}Ar$ age wherein the fluence monitor age is constrained independently of its K-Ar systematics (Merrihue & Turner, 1966), only the total decay constant. Using lower and upper bound values of EC_{ground}/β^+ corresponding to 150 and 212 as described above, the decay constants calculated by Min et al. (2000) ($\lambda_{EC*} = 0.580 \pm 0.014 \times 10^{-10}$ a^{-1} and $\lambda_T = 5.463 \pm 0.107 \times 10^{-10}$ a^{-1}), and the β^+/β^- from Engelkemeir et al. (1962) ($1.12 \pm 0.14 \times 10^{-5}$), we calculate a β^+ decay constant of $5.47 \pm 0.69 \times 10^{-15}$ a^{-1}, and a range of EC_{ground} decay constants of 8.2 - 11.6 $\times 10^{-13}$ a^{-1}. Combining these values with the Min et al. (2000) quantities yields a new partial decay constant for ^{40}K to ^{40}Ar (λ_{40Ar}) that ranges from 0.588-0.592 $\times 10^{-10}$ a^{-1} and total decay constant (λ_T) that ranges from 5.471-5.475 $\times 10^{-10}$ a^{-1}. These ranges are within the uncertainties calculated by Min et al. (2000) for decay constants that do not include the EC_{ground} decay mode. Existing and modified constraints on the decay modes are given in Table 1. Our preferred decay constants are those calculated with the $EC_{ground}/\beta^+ = 212$ from Mougeot (2018).

Table 1. Evaluations of decay mode branches and total decay constant used in age determination. λ_{40Ar} is the partial decay constant for the ^{40}Ar branch, including both the EC* and EC_{ground} components. Uncertainties from the β^+/β^- and EC_{ground}/β^+ do not substantially change the uncertainties in λ_{40Ar} or λ_T.

Parameter	Value ± 2σ	Relative Unc. (%)	References
Previous values			
λ_{EC*}	$0.580 \pm 0.014 \times 10^{-10}$ a^{-1}	2.4	Min et al. (2000)
λ_T	$5.463 \pm 0.107 \times 10^{-10}$ a^{-1}	2.0	Min et al. (2000)
$\lambda_{\beta+}$	$5.47 \pm 0.69 \times 10^{-15}$ a^{-1}	13	Engelkemeir et al. (1962)
Modified values with lower bound $EC_{ground}/\beta^+ = 150$			
$\lambda_{ECground}$	$8.2 \pm 1.0 \times 10^{-13}$ a^{-1}	13	This work
λ_{40Ar}	$0.588 \pm 0.014 \times 10^{-10}$ a^{-1}	2.4	This work
λ_T	$5.471 \pm 0.107 \times 10^{-10}$ a^{-1}	2.0	This work
Modified values with upper bound $EC_{ground}/\beta^+ = 212$			
$\lambda_{ECground}$	$11.6 \pm 1.5 \times 10^{-13}$ a^{-1}	13	This work
λ_{40Ar}	$0.592 \pm 0.014 \times 10^{-10}$ a^{-1}	2.4	This work
λ_T	$5.475 \pm 0.107 \times 10^{-10}$ a^{-1}	2.0	This work

Consequently, K-Ar (and $^{40}Ar/^{39}Ar$) ages calculated with these new decay constants will be younger than those calculated using the Min et al. (2000) decay constants. K-Ar dates are most sensitive to shifts in the decay constant because they incorporate the branching ratio, which is more strongly affected than the total ^{40}K decay constant. K-Ar ages will decrease by ~1.4-2.0 % at 1 Ma, ~1.1-1.5 % at 1 Ga, and ~0.6-0.8 % at 4.5 Ga (Figure 5). Ages determined using the $^{40}Ar/^{39}Ar$ method, for which the fluence monitor age is independently constrained (e.g., Kuiper et al., 2008; Rivera et al., 2011), are much less sensitive to the change in decay constant. Using equation 5 from Renne et al. (1998), and assuming calibration to a monitor with an age of 28.2 Ma, ages < 28 Ma increase only slightly, by < 0.002%. There is no age difference at 28.2 Ma, the fluence monitor age. Ages then decrease for ages > 28.2 Ma, with ages decreased by 0.07-0.10 % at 2.5 Ga, and by 0.09-0.13% at 4.5 Ga (Figure 5).

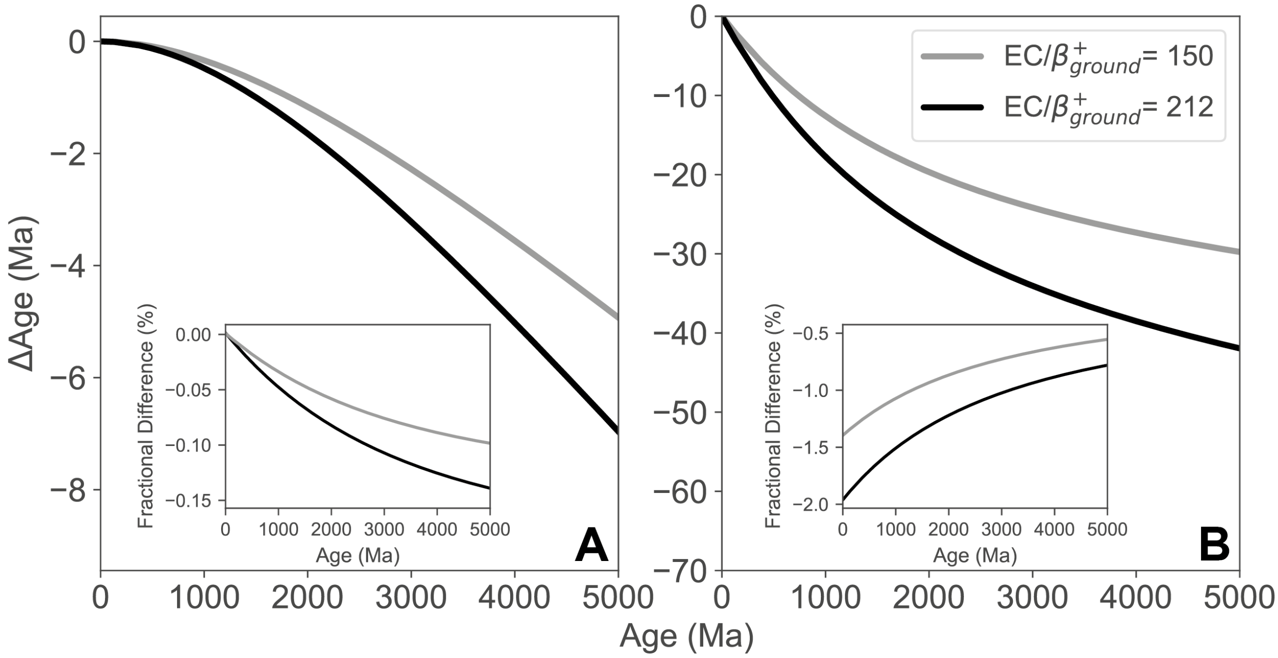

Figure 5. Change in age, Δage, is the age of a given sample with the decay mode to ground state included, subtracted from the age with the decay mode to ground state omitted. Panel A shows the change in age using the $^{40}Ar/^{39}Ar$ equation with independently calibrated standards using both the lower bound (EC/β^+ = 150; grey) and upper bound (EC/β^+ = 212; black). Panel B shows the change in age using the K-Ar equation using both the lower bound (EC/β^+ = 150; grey) and upper bound (EC/β^+ = 212; black). Inset figures in each panel show the fractional differences in age by the inclusion of both the upper and lower bound EC/β^+ value. The larger difference in ages for the K-Ar system is due to the dependence on both the total decay constant and branching ratio.

The age of fluence monitors such as the Fish Canyon tuff sanidine (e.g., Morgan et al., 2014) determined by intercomparison with astronomically tuned ages of ash beds (Kuiper et al., 2008; Rivera et al., 2011) is also sensitive to revision of decay constants. Using the data published by Kuiper et al. (2008), and incorporating an EC_{ground} decay mode, we calculate a new age for Fish Canyon sanidine of 28.200 ± 0.044 Ma, nominally lower, but indistinguishable from the published value of 28.201 ± 0.044 Ma. Overall, the effects of an EC_{ground} decay mode are unlikely to be significant for most current applications of $^{40}Ar/^{39}Ar$ geochronology. However, given the levels of analytical precision attainable by the K-Ar dating approach when dating geologically recent materials by K-Ar (e.g., Altherr et al. 2019), the EC_{ground} decay mode will impact the accuracy of this chronometer.

9. Conclusion

The Fermi theory of β decay has decades of experimental support and is well established. We demonstrate this here by using these theories to accurately calculate the decay rate of a ^{22}Na, a nuclide with an experimentally-verified decay rate. We have used this information to demonstrate the high likelihood that the suspected second electron capture decay mode of ^{40}K exists. Based on the calculations of Mougeot (2018), the best estimate of the partial decay constant for ^{40}K direct to ground state ^{40}Ar is be $11.6 \pm 1.5 \times 10^{-13}$ a^{-1} (2σ), and other calculations are no lower than about 8.2×10^{-13} a^{-1}. Combining this with the decay constants published by Min et al. (2000) results in revised values of $\lambda_{40Ar} = 0.592 \pm 0.014 \times 10^{-10}$ a^{-1} and $\lambda_T = 5.475 \pm 0.107 \times 10^{-10}$ a^{-1}. This addresses a longstanding question in K-Ar and $^{40}Ar/^{39}Ar$ geochronology and provides future workers with confidence that the ^{40}K EC_{ground} decay mode exists. Just as important as providing support for its existence, we also demonstrate that the magnitude of this decay mode is small enough that neglecting it has not yet resulted in significantly biased geochronological $^{40}Ar/^{39}Ar$ data. The same cannot be stated for the K-Ar dating approach, especially for geologically-young materials.

Despite the strong grounding in theory, the EC_{ground} decay mode has yet to be detected. The next step is experimental verification to determine the branching ratio. This will allow for a more complete evaluation of uncertainties associated with the decay mode and the branching ratio. This experiment is difficult, but not intractable.

10. Author contribution

The study was conceived by JC and RBI. JC, AC, and DS calculated the ratio of electron capture to beta activities and measured x-rays. JC, RBI, DFM and MMT calculated the effects for geochronology. JC wrote the manuscript with contributions from all authors.

Competing interests

The authors declare that they have no conflicts of interest.

Acknowledgements

JC studentship funded by the UK Space Agency grant number ST/P001289/1. NERC are thanked for continued funding of the National Environmental Isotope Facility (Ar/Ar laboratory) at SUERC NE/S011587/1. MMT acknowledges The Royal Society (NF171365) for funding. RBI thanks the members of the Geochron Club for discussion. We thank two anonymous reviewers who helped clarify and focus the manuscript, and Dr. Clare Warren for editorial handling.

References

Aldrich, L.T. and Nier, A.O., Argon 40 in potassium minerals, Phys. Rev., 74(8), 876-877, http://dx.doi.org/10.1103/PhysRev.74.876, 1948.

Altherr, R., Mertz-Kraus, R., Volker, F., Kreuzer, H., Henjes-Kunst, F. and Lange, U., Geodynamic setting of Upper Miocene to Quaternary alkaline basalts from Harrat al 'Uwayrid (NW Saudi Arabia): Constraints from KAr dating, chemical and Sr-Nd-Pb isotope compositions, and petrological modelling, Lithos, 330, 120-138, http://dx.doi.org/10.1016/j.lithos.2019.02.007, 2019.

Alvarez, L.W., Nuclear K electron capture, Phys. Rev., 52(2), 134-135, http://dx.doi.org/10.1103/PhysRev.52.134, 1937.

Audi, G., Bersillon, O., Blachot, J. and Wapstra, A.H., The NUBASE evaluation of nuclear and decay properties, Nucl. Phys. A, 729(1), 3-128, http://dx.doi.org/10.1016/j.nuclphysa.2003.11.001, 2003.

Baerg, A.P., Electron capture to positron branching ratios in the decay of ^{22}Na and ^{44}Sc, Can. J. Phys., 61(8), 1222-1226, http://dx.doi.org/10.1139/p83-155, 1983.

Bahcall, J.N., Electron Capture and Nuclear Matrix Elements of Be^{7}, Phys. Rev., 128(3), 1297-1301, http://dx.doi.org/10.1201/9780429502811-65, 1962.

Bambynek, W., Behrens, H., Chen, M.H., Crasemann, B., Fitzpatrick, M.L., Ledingham, K.W.D., Genz, H., Mutterer, M. and Intemann, R.L., Orbital electron capture by the nucleus, Rev. Mod. Phys., 49(1), 77-221, http://dx.doi.org/10.1103/RevModPhys.49.77, 1977.

Bé, M.-M., Chisté, V., Dulieu, C., Mougeot, X., Browne, E., Chechev, V., Kuzmenko, N., Kondev, F., Luca, A., Galan, M., Table of radionuclides (Vol. 5-A= 22 to 244), Mongraphie BIPM-5, https://hal-cea.archives-ouvertes.fr/cea-02476352/document, 2010.

Beckinsale, R.D. and Gale, N.H., A reappraisal of the decay constants and branching ratio of ^{40}K, Earth Planet. Sci. Lett., 6(4), 289-294, http://dx.doi.org/10.1016/0012-821X(69)90170-8, 1969.

Bethe, H.A. and Bacher, R.F., Nuclear physics A. Stationary states of nuclei, Rev. Mod. Phys., 8(2), .82-229, http://dx.doi.org/10.1103/RevModPhys.8.82, 1936.

Bosch, H.E., Davidson, J., Davidson, M. and Szybisz, L., The electron capture to positron emission ratios in the decay of ^{22}Na and ^{65}Zn, Z. Phys. A., 280(4), 321-327, http://dx.doi.org/10.1007/BF01435440, 1977.

Chen, J., Nuclear Data Sheets for A=40. Nuclear Data Sheets 140, 1–376, http://dx.doi.org/10.1016/j.nds.2017.02.001, 2017.

Cresswell, A.J., Carter, J., Sanderson, D.C.W., Dose rate conversion parameters: Assessment of nuclear data, Radiat. Meas., 120, 195–201, http://dx.doi.org/10.1016/j.radmeas.2018.02.007, 2018.

Cresswell, A.J., Sanderson, D.C.W., Carter, J., Review of nuclear data for naturally occurring radionuclides applied to environmental applications, Eur. Phys. J. Plus, 134(2), 69, http://dx.doi.org/10.1140/epjp/i2019-12437-1, 2019.

Di Stefano, P.C.F., Brewer, N., Fijałkowska, A., Gai, Z., Goetz, K.C., Grzywacz, R., Hamm, D., Lechner, P., Liu, Y., Lukosi, E. and Mancuso, M., The KDK (potassium decay) experiment. arXiv [preprint], arXiv:1711.04004, 10 November 2017.

Di Stefano, P.C.F., Brewer, N., Fijałkowska, A., Gai, Z., Goetz, K.C., Grzywacz, R., Hamm, D., Lechner, P., Liu, Y., Lukosi, E. and Mancuso, M., The KDK (potassium decay) experiment. J. Phys. Conf. Ser. (Vol. 1342, No. 1, 012062). IOP Publishing, http://dx.doi.org/10.1088/1742-6596/1342/1/012062, 2020.

Emery, G.T., Ionization through Nuclear Electron Capture and Internal Conversion, in: Atomic Inner-Shell Processes, Academic Press, New York, 201–231, http://dx.doi.org/10.1016/B978-0-12-196901-1.50010-8, 1975.

Engelkemeir, D.W., Flynn, K.F. and Glendenin, L.E., Positron Emission in the Decay of K^{40}, Phys. Rev., 126(5), 1818-1822, http://dx.doi.org/10.1103/PhysRev.126.1818, 1962.

Endt, P.M., Energy levels of A = 21–44 nuclei (VII), Nucl. Phys. A 521, 1–400, http://dx.doi.org/10.1016/0375-9474(90)90598-G, 1990.

Endt, P.M. and Van der Leun, C., Energy levels of A= 21− 44 nuclei (V). Nucl. Phys. A, 214, 1-625, http://dx.doi.org/10.1016/0375-9474(73)91131-7, 1973.

Endt, P.M. and Van der Leun, C., Energy levels of A= 21–44 nuclei (VI). Nucl. Phys. A, 310(1-2), 1-751, http://dx.doi.org/10.1016/0375-9474(78)90611-5, 1978,

ENSDF Collaboration, LOGFT, http://www.nndc.bnl.gov/nndcscr/ensdf_pgm/ analysis/logft/unx/.

Fermi, E., Versuch einer Theorie der β-Strahlen. I, Z. Phys., 88, 161-177, http://dx.doi.org/10.1007/BF01351864, 1934.

Fireman, E.L., On the Decay of K^{40}, Phys. Rev., 75(9), 1447, http://dx.doi.org/10.1103/PhysRev.75.1447.2, 1949.

Forbes, G.B., Gallup, J. and Hursh, J.B., Estimation of total body fat from potassium-40 content, Science, 133(3446), 101-102., http://dx.doi.org/10.1126/science.133.3446.101, 1961.

Garner, E.L., Murphy, T.J., Gramlich, J.W., Paulsen, P.J., Barnes, I.L., Absolute isotopic abundance ratios and the atomic weight of a reference sample of potassium, J. Res. Natl. Bur. Stand. A Phys. Chem.: Vols., 79A(6), 713-725, http://dx.doi.org/10.6028/jres.079A.028, 1975.

Huber, P., Determination of antineutrino spectra from nuclear reactors, Phys. Rev. C, 84(2), 024617, http://dx.doi.org/10.1103/PhysRevC.84.024617, 2011.

Kossert, K. and Günther, E., LSC measurements of the half-life of ^{40}K, Appl. Radiat. Isot., 60(2-4), 459-464, http://dx.doi.org/10.1016/j.apradiso.2003.11.059, 2004.

Krane, K.S., Halliday, D., 3rd ed., Introductory nuclear physics, Wiley, New York, 845pp., 1987.

Kreger, W.E., K Capture to positron ratio for Na^{22}, Phys. Rev., 96(6), 1554-1555, http://dx.doi.org/10.1103/PhysRev.96.1554, 1954.

Kuiper, K.F., Deino, A., Hilgen, F.J., Krijgsman, W., Renne, P.R., Wijbrans, J.R., Synchronizing rock clocks of Earth history, Science, 320(5875), 500-504, http://dx.doi.org/10.1126/science.1154339, 2008.

Kunze, V., Schmidt-Ott, W.D. and Behrens, H., Remeasurement of capture to positron decay ratios in ^{22}Na and ^{65}Zn and comparison with theory, Z. Phys. A, 337(2), 169-173, http://dx.doi.org/10.1007/BF01294288, 1990.

Leutz, H., Schulz, G. and Wenninger, H., The decay of potassium-40, Z. Phys., 187(2), 151-164, http://dx.doi.org/10.1007/BF01387190, 1965.

MacMahon, T.D. and Baerg, A.P., The electron capture to positron branching ratio in the decay of ^{22}Na, Can. J. Phys., 54(14), 1433-1437, http://dx.doi.org/10.1139/p76-168, 1976.

Malonda, A.G. and Carles, A.G., Half-life determination of ^{40}K by LSC, Appl. Radiat. Isot., 56(1-2), 153-156, http://dx.doi.org/10.1016/S0969-8043(01)00181-6, 2002.

Marshall, B.D., DePaolo, D.J., Precise age determinations and petrogenetic studies using the K-Ca method, Geochim. Cosmochim. Acta, 46(12), 2537–2545, http://dx.doi.org/10.1016/0016-7037(82)90376-3, 1982.

McCann, M.F., Smith, K.M., Direct measurement of the K electron capture to positron emission ratio in the decay of ^{22}Na, J. Phys. A Gen. Phys., 2(3), 392–397, http://dx.doi.org/10.1088/0305-4470/2/3/018, 1969.

McDougall, I., Harrison, T.M., 2nd ed., Geochronology and Thermochronology by the ^{40}Ar/^{39}Ar Method, Oxford University Press, Oxford. 269, 1999.

Merrihue, C. and Turner, G., Potassium-argon dating by activation with fast neutrons, J. Geophys. Res. Solid Earth, 71(11), 2852-2857, http://dx.doi.org/10.1029/JZ071i011p02852, 1966.

Min, K., Mundil, R., Renne, P.R. and Ludwig, K.R., A test for systematic errors in ^{40}Ar/^{39}Ar geochronology through comparison with U/Pb analysis of a 1.1-Ga rhyolite, Geochim. Cosmochim. Acta, 64(1), 73-98, http://dx.doi.org/10.1016/S0016-7037(99)00204-5, 2000.

Morgan, L.E., Mark, D.F., Imlach, J., Barfod, D. and Dymock, R., FCs-EK: A new sampling of the Fish Canyon Tuff 40Ar/39Ar neutron flux monitor, Geol. Soc. Spec. Publ., 378(1), 63-67, http://dx.doi.org/10.1144/SP378.21, 2014.

Mougeot, X., Helmer, R.G., ^{40}K – Comments on evaluation of decay data, LNHB/ INEEL, http://www.nucleide.org/DDEP_WG/Nuclides/K-40_com.pdf, 2009.

Mougeot, X., Improved calculations of electron capture transitions for decay data and radionuclide metrology,Appl. Radiat. Isot., 134, 225-232, http://dx.doi.org/10.1016/j.apradiso.2017.07.027, 2018.

Nähle, O., Kossert, K. and Klein, R., Activity standardization of 22Na, Appl. Radiat. Isot., 66(6-7), 865-871, http://dx.doi.org/10.1016/j.apradiso.2008.02.028, 2008.

Patterson, C., Age of meteorites and the earth, Geochim. Cosmochim. Acta, 10(4), 30-237, http://dx.doi.org/10.1016/0016-7037(56)90036-9, 1956.

Pradler, J., Singh, B. and Yavin, I., On an unverified nuclear decay and its role in the DAMA experiment, Phys. Lett. B, 720(4-5), 399-404, http://dx.doi.org/10.1016/j.physletb.2013.02.033, 2013.

Preece, K., Mark, D.F., Barclay, J., Cohen, B.E., Chamberlain, K.J., Jowitt, C., Vye-Brown, C., Brown, R.J. and Hamilton, S., Bridging the gap: $^{40}Ar/^{39}Ar$ dating of volcanic eruptions from the 'Age of Discovery', Geology, 46(12), 1035-1038, http://dx.doi.org/10.1130/G45415.1, 2018.

Renne, P.R., Sharp, W.D., Deino, A.L., Orsi, G. and Civetta, L., $^{40}Ar/^{39}Ar$ dating into the historical realm: Calibration against Pliny the Younger, Science, 277(5330), 1279-1280, http://dx.doi.org/10.1126/science.277.5330.1279, 1997.

Renne, P.R., Swisher, C.C., Deino, A.L., Karner, D.B., Owens, T.L. and DePaolo, D.J., Intercalibration of standards, absolute ages and uncertainties in $^{40}Ar/^{39}Ar$ dating, Chem. Geol., 145(1-2), 117-152, http://dx.doi.org/10.1016/S0009-2541(97)00159-9, 1998.

Renne, P.R., $^{40}Ar/^{39}Ar$ age of plagioclase from Acapulco meteorite and the problem of systematic errors in cosmochronology. Earth Planet. Sci. Lett., 175(1-2), 13-26, http://dx.doi.org/10.1016/S0012-821X(99)00287-3, 2000.

Renne, P.R., Mundil, R., Balco, G., Min, K. and Ludwig, K.R., Joint determination of ^{40}K decay constants and $^{40}Ar*/^{40}K$ for the Fish Canyon sanidine standard, and improved accuracy for $^{40}Ar/^{39}Ar$ geochronology, Geochim. Cosmochim. Acta,74(18), 5349-5367, http://dx.doi.org/10.1016/j.gca.2010.06.017, 2010.

Renne, P.R., Balco, G., Ludwig, K.R., Mundil, R., Min, K., Response to the comment by W.H. Schwarz et al. on "Joint determination of ^{40}K decay constants and $^{40}Ar*/^{40}K$ for the Fish Canyon sanidine standard, and improved accuracy for $^{40}Ar/^{39}Ar$ geochronology" by P.R. Renne et al. (2010), Geochim. Cosmochim. Acta, 75, 5097–5100, http://dx.doi.org/10.1016/j.gca.2011.06.021, 2011.

Rivera, T.A., Storey, M., Zeeden, C., Hilgen, F.J., Kuiper, K., A refined astronomically calibrated $^{40}Ar/^{39}Ar$ age for Fish Canyon sanidine, Earth Planet. Sci. Lett., 311, 420–426, http://dx.doi.org/10.1016/j.epsl.2011.09.017, 2011.

Schmidt-Ott, W.-D., Lauerwald, J., Bosch, U., Dornh6fer, H., Schrewe, U.J., Behrens, H., Electron-capture to positron ratio in the decays of ^{22}Na and ^{65}Zn: Proceedings of the 7th International Conference on Atomic Masses and Fundamental Constants AMCO-7, Darmstadt: Technische Hochschule Darmstadt, Lehrdruckerei, 3- 7 September 1984.

Steiger, R. and Jäger, E., Subcommission on geochronology: convention on the use of decay constants in geo-and cosmochronology, Earth Planet. Sci. Lett., 36(3), 359-362, http://dx.doi.org/10.1016/0012-821X(77)90060-7, 1977.

Stukel, M.: Characterization Of Large Area Avalanche Photodiodes For The Measurement Of The Electron Capture Decay Of ^{40}K To The Ground State Of ^{40}Ar. M.Sc. Thesis, Queen's University. 159 pp., 2018.

Sýkora, I. and Povinec, P., Measurement of electron capture to positron emission ratios in light and medium nuclides, Nucl. Instrum. Methods Phys. Res. B, 17(5-6), 467-471, http://dx.doi.org/10.1016/0168-583X(86)90189-8, 1986.

Vatai, E., Varga, D. and Uchrin, J., Measurement of the $\epsilon/\beta+$ ratio in the decay of ^{22}Na and ^{74}As, Nucl. Phys. A, 116(3), 637-642, http://dx.doi.org/10.1016/0375-9474(68)90396-5, 1968.

Wang, M., Audi, G., Kondev, F.G., Huang, W.J., Naimi, S., Xu, X., The AME2016 atomic mass evaluation (II). Tables, graphs and references, Chinese Phys. C 41(3), 030003, https://doi.org/10.1088/1674-1137/41/3/030003, 2017.

Wasserburg, G.J. and Hayden, R.J., A^{40}-K^{40} dating. Geochim. Cosmochim. Acta, 7(1-2), 51-60, http://dx.doi.org/10.1016/0016-7037(55)90045-4, 1955.

Williams, A., Measurement of the ratio of electron capture to positon emission in the decay of Na-22, Nucl. Phys., 52, 324-332, http://dx.doi.org/10.1016/0029-5582(64)90696-0, 1964.

Yukawa, H. and Sakata, S., On the Theory of the β-Disintegration and the Allied Phenomenon, Proc. Phys. Math. Soc. Jpn., 3rd Series, 17, 467-479, https://www.jstage.jst.go.jp/article/ppmsj1919/17/0/17_0_467/_pdf, 1935.