ArAR – Argon Age Recalculator: Documentation

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Calculations

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Contents

The *ArAR* software is designed to make "recalculating" previously published (i.e. *legacy*) K-Ar and $^{40}Ar/^{39}Ar$ dates relatively rapid and straightforward. However, it is imperative that the user fully understands the theory behind the *ArAR* algorithms and how legacy dates are converted to account for different values of ^{40}K decay constants, K isotopic abundances, and monitor mineral ages. In the following sections, I derive the equations employed in the *ArAR* software, and I provide notes on how the equations are actually implemented to clarify how values entered in the *ArAR* graphical user interface (GUI) are processed. For more details on how to use the *ArAR* software, see the Manual. All mathematical symbols employed here for quantities that are are used in the main *ArAR* GUI are consistent with those described in the Nomenclature. Additional symbols are explained as needed.

1 Recalculating Legacy K-Ar Dates

1.1 Theory

The general age equation for the K-Ar system is given by

$$t = \frac{1}{\lambda} \log_e \left[\frac{\lambda}{\lambda_{^{40}Ar}} \frac{^{40}Ar^*}{^{40}K} + 1 \right], \tag{1.1}$$

where t is the age, λ is the total decay constant for ^{40}K , $\lambda_{^{40}Ar}$ is the partial decay constant for ^{40}K that accounts for the production of ^{40}Ar (note that the quantity $\lambda/\lambda_{^{40}Ar}$ is the inverse of the ^{40}K decay branching ratio, which describes the fraction of decays of ^{40}K that produce $^{40}Ar^*$), $^{40}Ar^*/^{40}K$ is the measured ratio of radiogenic ^{40}Ar to ^{40}K , and $\log_e[\cdot]$ is the natural logarithm (Dalrymple and Lanphere, 1969). Hence, a previously published K-Ar date, t_o, may be expressed by

$$t_o = \frac{1}{\lambda_o} \log_e \left[\frac{\lambda_o}{\lambda_{^{40}Ar_o}} \frac{^{40}Ar^*_o}{^{40}K_o} + 1 \right], \tag{1.2}$$

where the subscript o denotes the values that were originally used to calculate t_o.

If the measured values for $^{40}Ar^*_o$ and $^{40}K_o$, or the molar ratio $^{40}Ar^*_o/^{40}K_o$, are unavailable or too little information was given to directly calculate a K-Ar date using these values and Eq. (1.1), then

we may rearrange Eq. (1.2) to obtain

$$\frac{^{40}Ar^*_o}{^{40}K_o} = \frac{\lambda_{^{40}Ar_o}}{\lambda_o}(\exp[\lambda_o t_o] - 1). \tag{1.3}$$

A "new" $^{40}Ar^*/^{40}K$ ratio may be calculated by multiplying both sides of Eq. (1.3) by the (dimensionless) factor

$$\frac{^{40}K_{ao}}{^{40}K_a},$$

where

$$^{40}K_{ao} \equiv \frac{^{40}K_o}{K}, \text{ and } ^{40}K_a \equiv \frac{^{40}K}{K}$$

are the "old" and "new" values for the isotopic abundance of ^{40}K relative to total K, K, respectively. Thus,

$$\frac{^{40}Ar^*_o}{^{40}K_o}\frac{^{40}K_{ao}}{^{40}K_a} = \frac{^{40}Ar^*_o}{^{40}K_o}\frac{^{40}K_o}{K}\frac{K}{^{40}K} = \frac{^{40}K_{ao}}{^{40}K_a}\frac{\lambda_{^{40}Ar_o}}{\lambda_o}(\exp[\lambda_o t_o] - 1), \tag{1.4}$$

and since $^{40}Ar^*_o = {}^{40}Ar^*$ (because the number of atoms of radiogenic ^{40}Ar* that were measured is invariant), Eq. (1.4) reduces to

$$\frac{^{40}Ar^*}{^{40}K} = \frac{^{40}K_{ao}}{^{40}K_a}\frac{\lambda_{^{40}Ar_o}}{\lambda_o}(\exp[\lambda_o t_o] - 1). \tag{1.5}$$

In effect, the $^{40}Ar^*/^{40}K$ ratio has been "updated" to account for any changes in the values for the isotopic abundance of ^{40}K . Substituting Eq. (1.5) into Eq. (1.1), we obtain a "new" date

$$\boxed{t = \frac{1}{\lambda}\ \log_e\left[\frac{^{40}K_{ao}}{^{40}K_a}\frac{\lambda_{^{40}Ar_o}}{\lambda_o}\frac{\lambda}{\lambda_{^{40}Ar}}(\exp[\lambda_o t_o] - 1) + 1\right].} \tag{1.6}$$

This expression fully accounts for changes in the accepted values for the total decay constant and branching ratio of ^{40}K, as well as changes in the accepted value for the isotopic abundance of ^{40}K. Note, Eq. (1.6) is a simple generalization of Eq. (2) given by Dalrymple (1979).

1.2 Propagation of Uncertainty

When recalculating K-Ar dates with Eq. (1.6), there are several sources of uncertainty from: (1) the previously published date, $t_o \pm \sigma_{t_o}$; (2) the relative isotopic abundance of ^{40}K : (a) $^{40}K_{ao} \pm \sigma_{^{40}K_{ao}}$, and (b) $^{40}K_a \pm \sigma_{^{40}K_a}$; and (3) the decay constants for ^{40}K : (a) $\lambda_{^{40}Ar_o} \pm \sigma_{\lambda_{^{40}Ar_o}}$, (b) $\lambda_{^{40}Ar} \pm \sigma_{\lambda_{^{40}Ar}}$, (c) $\lambda_o \pm \sigma_{\lambda_o}$, and (d) $\lambda \pm \sigma_\lambda$. Of these, only σ_{t_o} is an "internal" source of uncertainty, while $\sigma_{^{40}K_{ao}}$, $\sigma_{^{40}K_a}$, $\sigma_{\lambda_{^{40}Ar_o}}$, $\sigma_{\lambda_{^{40}Ar}}$, σ_{λ_o}, and σ_λ are "external" sources of uncertainty. In *ArAR*, the internal uncertainties in the legacy data are always propagated into the recalculated K-Ar dates, and the

user has the option of propagating external uncertainties (from either the K isotopic abundances, the ^{40}K decay constants, or both). In addition, the user may specify whether error propagation should be carried out analytically or by the Monte Carlo method. See the Manual for details on how to select these options.

1.2.1 Analytical Method

If a set of N measured quantities $x_1, x_2, ..., x_N$ with the independent and random uncertainties $\sigma_{x_1}, \sigma_{x_2}, ..., \sigma_{x_N}$ are used to calculate the value of a function $f(x_1, x_2, ..., x_N)$, then the uncertainty in f is given by

$$\sigma_f = \sqrt{\left(\frac{\partial f}{\partial x_1}\sigma_{x_1}\right)^2 + \left(\frac{\partial f}{\partial x_2}\sigma_{x_2}\right)^2 + \cdots + \left(\frac{\partial f}{\partial x_N}\sigma_{x_N}\right)^2}. \tag{1.7}$$

I have employed this general equation (Taylor, 1997, p. 75) in *ArAR* for propagating uncertainties analytically during recalculation of legacy K-Ar and ^{40}Ar/^{39}Ar dates. Equation (1.6) is a function with seven sources of uncertainty, i.e., $t = f(t_o, {}^{40}K_{ao}, {}^{40}K_a, \lambda_{^{40}Ar_o}, \lambda_{^{40}Ar}, \lambda_{\beta_o}, \lambda_\beta)$. (Recall without loss of generality that $\lambda \equiv \lambda_{^{40}Ar_o} + \lambda_\beta$.) Therefore, a recalculated K-Ar date has the uncertainty

$$\begin{aligned}\sigma_t = \Bigg[&\left(\frac{\partial t}{\partial t_o}\sigma_{t_o}\right)^2 + \left(\frac{\partial t}{\partial\, {}^{40}K_{ao}}\sigma_{^{40}K_{ao}}\right)^2 + \left(\frac{\partial t}{\partial\, {}^{40}K_a}\sigma_{^{40}K_a}\right)^2 \\ &+ \left(\frac{\partial t}{\partial \lambda_{^{40}Ar_o}}\sigma_{\lambda_{^{40}Ar_o}}\right)^2 + \left(\frac{\partial t}{\partial \lambda_{^{40}Ar}}\sigma_{\lambda_{^{40}Ar}}\right)^2 + \left(\frac{\partial t}{\partial \lambda_{\beta_o}}\sigma_{\lambda_{\beta_o}}\right)^2 + \left(\frac{\partial t}{\partial \lambda_\beta}\sigma_{\lambda_\beta}\right)^2 \Bigg]^{1/2}.\end{aligned} \tag{1.8}$$

The partial differential equations from each of the seven terms in Eq. (1.8) are provided below, and even though I have omitted their derivation here, the interested reader is encouraged to consult texts such as Boas (2006) or Rogawski (2008) for details on partial differentiation.

$$\frac{\partial t}{\partial t_o} = \frac{\alpha\lambda_o e^{\lambda_o t_o}}{\lambda(\alpha(e^{\lambda_o t_o} - 1) + 1)}, \tag{1.9a}$$

$$\text{where } \alpha \equiv \frac{\lambda_{^{40}Ar_o}}{\lambda_o}\frac{\lambda}{\lambda_{^{40}Ar}}\frac{{}^{40}K_{ao}}{{}^{40}K_a}.$$

$$\frac{\partial t}{\partial\, {}^{40}K_{ao}} = \frac{\eta}{\lambda\,(\eta\, {}^{40}K_{ao} + 1)}, \tag{1.9b}$$

$$\text{where } \eta \equiv \frac{\lambda_{^{40}Ar_o}}{\lambda_o}\frac{\lambda}{\lambda_{^{40}Ar}}\frac{(e^{\lambda_o t_o} - 1)}{{}^{40}K_a}.$$

$$\frac{\partial t}{\partial\, {}^{40}K_a} = \frac{-\eta'}{\lambda\ {}^{40}K_a(\eta' + {}^{40}K_a)}, \tag{1.9c}$$

$$\text{where } \eta' \equiv \frac{\lambda_{^{40}Ar_o}}{\lambda_o}\frac{\lambda}{\lambda_{^{40}Ar}}\,{}^{40}K_{ao}(e^{\lambda_o t_o}-1).$$

$$\frac{\partial t}{\partial \lambda_{^{40}Ar_o}} = \frac{\lambda_{\beta_o}\left(e^{\lambda t}-1\right)+\gamma\lambda^2_{^{40}Ar_o}t_o e^{\lambda_o t_o}}{\lambda_{^{40}Ar_o}\lambda_o\lambda e^{\lambda t}}, \tag{1.9d}$$

$$\text{where } \gamma \equiv \frac{^{40}K_{ao}}{^{40}K_a}\frac{\lambda}{\lambda_{^{40}Ar}}.$$

$$\frac{\partial t}{\partial \lambda_{^{40}Ar}} = -\frac{\gamma'\lambda_\beta+\lambda^2_{^{40}Ar}t}{\lambda^2_{^{40}Ar}\lambda e^{\lambda t}}, \tag{1.9e}$$

$$\text{where } \gamma' \equiv \frac{^{40}K_{ao}}{^{40}K_a}\frac{\lambda_{^{40}Ar_o}}{\lambda_o}(e^{\lambda_o t_o}-1).$$

$$\frac{\partial t}{\partial \lambda_{\beta_o}} = \frac{\varphi t_o e^{\lambda_o t_o}-e^{\lambda t}+1}{\lambda_o\lambda e^{\lambda t}}, \tag{1.9f}$$

$$\text{where } \varphi \equiv \frac{^{40}K_{ao}}{^{40}K_a}\frac{\lambda}{\lambda_{^{40}Ar}}\lambda_{^{40}Ar_o}.$$

$$\frac{\partial t}{\partial \lambda_\beta} = \frac{\varphi' e^{-\lambda t}-t}{\lambda}, \tag{1.9g}$$

$$\text{where } \varphi' \equiv \frac{^{40}K_{ao}}{^{40}K_a}\frac{\lambda_{^{40}Ar_o}}{\lambda_o}\frac{(e^{\lambda_o t_o}-1)}{\lambda_{^{40}Ar}}.$$

In *ArAR*, Eqs. (1.9) are computed for each recalculated K-Ar date and the results are substituted into Eq. (1.8). If any external sources of uncertainty are excluded by the user, then the corresponding values (i.e., $\sigma_{^{40}K_{ao}}$, $\sigma_{^{40}K_a}$, $\sigma_{\lambda_{^{40}Ar_o}}$, $\sigma_{\lambda_{^{40}Ar}}$, σ_{λ_o}, and/or σ_λ) are set to zero. This effectively reduces the number of terms that contribute to the uncertainty of the recalculated K-Ar date (the uncertainty in t_o is always propagated).

1.2.2 Monte Carlo Method

In abstract, the Monte Carlo method relies on the repeated sampling of large populations of values representing distinct quantities to compute a population of results using some predefined mathematical combination of the sample values. Inferences can then be made on the population of results using descriptive statistics.

Because Eq. (1.6) is a function of seven variables, synthetic populations are generated for each variable (t_o, $^{40}K_{ao}$, $^{40}K_a$, $\lambda_{^{40}Ar_o}$, $\lambda_{^{40}Ar}$, λ_{β_o}, and λ_β). Each synthetic population contains pseudo-

random numbers that are normally distributed[1] about a central value (e.g., t_o) with standard deviation equal to the uncertainty in the central value (e.g., σ_{t_o}). Each synthetic population has the same size (i.e., the number of values in each population is the same), which can be specified in the main *ArAR* GUI (see the Manual for details on how to edit the size of the synthetic populations). If the uncertainty for a particular variable is set to zero (e.g., if $\sigma_{\lambda_{^{40}Ar}} = 0$ because external uncertainties from the ^{40}K decay constants are not being propagated), then every member of the synthetic population for that variable will equal the mean value of the variable (e.g., all values in the synthetic population for $\lambda_{^{40}Ar}$ will be identically equal to $\lambda_{^{40}Ar}$).

Once the seven synthetic populations are generated for t_o, $^{40}K_{ao}$, $^{40}K_a$, $\lambda_{^{40}Ar_o}$, $\lambda_{^{40}Ar}$, λ_{β_o}, and λ_β (with standard devaitions given by σ_{t_o}, $\sigma_{^{40}K_{ao}}$, $\sigma_{^{40}K_a}$, $\sigma_{\lambda_{^{40}Ar_o}}$, $\sigma_{\lambda_{^{40}Ar}}$, $\sigma_{\lambda_{\beta_o}}$, and σ_{λ_β}, respectively), a synthetic 'results' population of recalculated K-Ar dates is generated in the following way: (1) a single value is randomly drawn from each of the seven source populations[2]; (2) the total decay constants, λ_o and λ, are calculated; (3) a synthetic recalculated K-Ar date is computed using Eq. (1.6) and is stored in the results population; (4) steps 1–3 are repeated until the results population has the size specified in the main *ArAR* GUI. The results population is normally distributed about a central value[3], and the uncertainty can be inferred simply by calculating the sample standard deviation:

$$\sigma_t = \sqrt{\frac{1}{N-1}\sum_{i=1}^{N}(t_i - \bar{t})^2},$$

where N is the size of the results population, the subscript i represents an individual value in the population, and

$$\bar{t} \equiv \frac{1}{N}\sum_{i=1}^{N} t_i$$

is the mean of the results population. The value of σ_t is returned when errors are propagated by the Monte Carlo method.

1.3 Implementation Notes

If K-Ar dates are entered in units of ka or Ga, they are first converted to units of Ma for calculations. The ^{40}K decay constants must be entered with units of a^{-1}, and they are converted to units of Ma^{-1} for calculations. After the K-Ar dates have been recalculated, they are converted

[1] The values in each synthetic population are drawn from a Gaussian, or 'normal,' limiting distribution.

[2] Note: every value in the synthetic source populations has an equal probability of being drawn, and the values are not removed permanently.

[3] The mean of the results population will be close to the analytically recalculated K-Ar date. As the population size approaches infinity, the mean value of the results population will converge on the analytical result. Note, however, that *ArAR always* returns the analytical result for the recalculated K-Ar date, and only uses the synthetic results population to infer an uncertainty in the recalculated date.

back to their original units (i.e., ka or Ga).

If the total ^{40}K decay constant, e.g., λ, is determined automatically from the partial decay constants, e.g., $\lambda_{^{40}Ar}$ and λ_β, then the uncertainty, e.g., σ_λ, is determined by analytical error propagation (see Eq. (1.7)).

2 Recalculating Legacy ^{40}Ar/^{39}Ar Dates

2.1 Theory

The general ^{40}Ar/^{39}Ar age equation is

$$t = \frac{1}{\lambda}\ \log_e\left[J\left(\frac{^{40}Ar^*}{^{39}Ar_K}\right)_s + 1\right], \tag{2.1}$$

where t is the age, λ is the total decay constant for ^{40}K, $(^{40}Ar^*/^{39}Ar_K)_s$ is the measured ratio of radiogenic ^{40}Ar to reactor-produced ^{39}Ar in the sample, and J is a dimensionless parameter, commonly called the irradiation parameter, defined as

$$J \equiv \frac{^{39}K}{^{40}K}\frac{\lambda}{\lambda_{^{40}Ar}}\Delta T \int dE\ \phi(E)\sigma(E), \tag{2.2}$$

where ^{39}K and ^{40}K are the number of atoms of ^{39}K and ^{40}K, respectively, that are in the monitor mineral, $\lambda_{^{40}Ar}$ is the partial decay constant for ^{40}K that accounts for the production of ^{40}Ar by radioactive decay, ΔT is the duration of the irradiation, $\phi(E)$ is the flux of neutrons with energy E, and $\sigma(E)$ is the neutron capture cross section at energy E for the ^{39}K(n,p)^{39}Ar reaction (Mitchell, 1968; McDougall and Harrison, 1999). Since it is problematic to accurately determine the fast-neutron dose that a sample has received (i.e., ΔT, $\phi(E)$, and $\sigma(E)$ are difficult to constrain), it is common practice to co-irradiate a K-bearing monitor mineral that has a well known age with the unknown sample. By rearranging Eq. (2.1), the irradiation parameter can be written as

$$J = \frac{\exp[\lambda t_m] - 1}{(^{40}Ar^*/^{39}Ar_K)_m}, \tag{2.3}$$

where t_m is the age of the monitor mineral, and $(^{40}Ar^*/^{39}Ar_K)_m$ is the measured ratio of radiogenic ^{40}Ar to reactor-produced ^{39}Ar in the monitor mineral.

From Eq. (2.1), a previously published ^{40}Ar/^{39}Ar date, t_o, may be expressed by

$$t_o = \frac{1}{\lambda_o}\ \log_e\left[J_o\left(\frac{^{40}Ar^*}{^{39}Ar_K}\right)_s + 1\right], \tag{2.4}$$

where the subscript o denotes the values that were originally used to calculate t_o. Note that the measured quantity $({}^{40}Ar^*/{}^{39}Ar_K)_s$ is invariant, since any change in the decay constants or isotopic abundance values for K will not change the number of atoms of ^{39}Ar and ^{40}Ar that were counted during the original mass spectrometry. Thus, we simply need to express the "old" J_o value in terms of a "new" J, solve Eq. (2.4) for $({}^{40}Ar/{}^{39}Ar_K)_s$, and substitute the result into the general ^{40}Ar/^{39}Ar age equation, Eq. (2.1).

If the sample was co-irradiated with a K-bearing monitor mineral, and if the monitor age, t_{m_o}, was reported along with the legacy date, t_o, then we may adopt Eq. (2.3) to write

$$J_o = \frac{\exp[\lambda_o t_{m_o}] - 1}{({}^{40}Ar^*/{}^{39}Ar_K)_m}. \tag{2.5}$$

Note again that the measured quantity $({}^{40}Ar^*/{}^{39}Ar_K)_m$ is invariant with respect to changes in accepted values for the decay constants or isotopic abundance values of K. Solving Eq. (2.3) for the $({}^{40}Ar^*/{}^{39}Ar_K)_m$ and substituting the result into Eq. (2.5), we obtain

$$J_o = J\,\frac{\exp[\lambda_o t_{m_o}] - 1}{\exp[\lambda t_m] - 1}. \tag{2.6}$$

We may then substitute Eq. (2.6) into Eq. (2.4) and solve for $({}^{40}Ar/{}^{39}Ar_K)_s$ to obtain

$$\left(\frac{{}^{40}Ar^*}{{}^{39}Ar_K}\right)_s = \frac{\exp[\lambda t_m] - 1}{\exp[\lambda_o t_{m_o}] - 1}\,\frac{\exp[\lambda_o t_o] - 1}{J}. \tag{2.7}$$

Notice that there are now two separate references to the age of the monitor mineral, namely t_{m_o} and t_m. While the monitor mineral that was used in the original analysis certainly has not changed, the accepted value for the age of that monitor mineral may have changed (e.g., due to "new" values for the decay constants and isotopic abundances of K, or from more recent experiments), and the revised value must be accounted for. Finally, by substituting Eq. (2.7) into Eq. (2.1), we arrive at an expression for the "new" date

$$\boxed{t = \frac{1}{\lambda}\,\log_e\left[\frac{\exp[\lambda t_m] - 1}{\exp[\lambda_o t_{m_o}] - 1}(\exp[\lambda_o t_o] - 1) + 1\right].} \tag{2.8}$$

Note that the irradiation parameter, J, is absent from Eq. (2.8) since it was in the numerator in Eq. (2.1) and in the denominator in Eq. (2.7), causing them to cancel to unity. Thus, it is not necessary to know the J value in order to recalculate a legacy ^{40}Ar/^{39}Ar date! Only the age of the monitor mineral used to calculate the legacy date is required to determine a "new" ^{40}Ar/^{39}Ar date. If the monitor age was not reported with the legacy date, but the original irradiation parameter, J_o,

and the quantity $({}^{40}Ar^*/{}^{39}Ar_K)_m$ were reported, then the original value for the monitor age may be calculated by rearranging Eq. (2.5) to write

$$t_{m_o} = \frac{1}{\lambda_o} \log_e \left[J_o \left(\frac{{}^{40}Ar^*}{{}^{39}Ar_K} \right)_m + 1 \right]. \tag{2.9}$$

2.2 *Equivalency with the K-Ar Recalculation Equation, Eq. (1.6)*

Adopting Eq. (2.5) as the starting expression for J_o when recalculating a legacy $^{40}\mathrm{Ar}/^{39}\mathrm{Ar}$ date is an arbitrary choice beyond the fact that it is common practice for researchers to use monitor minerals to calculate the irradiation parameter. An equivalent approach is to adopt an expression with the form of Eq. (2.2) for the irradiation parameter

$$J_o = \frac{{}^{39}K}{{}^{40}K_o} \frac{\lambda_o}{\lambda_{{}^{40}Ar_o}} \Delta T \int dE\ \phi(E)\sigma(E). \tag{2.10}$$

Notice that I have not added the subscript o to $^{39}\mathrm{K}$. This is because the production of $^{39}\mathrm{Ar_K}$ by the $^{39}\mathrm{K(n,p)}^{39}\mathrm{Ar}$ reaction during neutron irradiation of the monitor mineral is described by

$${}^{39}Ar_K = {}^{39}K \Delta T \int dE\ \phi(E)\sigma(E), \tag{2.11}$$

and since the measured quantity $({}^{40}Ar^*/{}^{39}Ar_K)_m$ is invariant, then the right-hand side of this expression is also invariant. In other words, the number of atoms of $^{39}\mathrm{Ar}$ that were produced in the monitor mineral during the irradiation and subsequently counted during mass spectrometry is independent of any changes we may consider for the values of the decay constants or isotopic abundances of K. Therefore, we can solve Eq. (2.2) for the invariant quantity ${}^{39}K\Delta T \int dE\ \phi(E)\sigma(E)$ and substitute it into Eq. (2.10) to obtain

$$J_o = J \frac{{}^{40}K}{{}^{40}K_o} \frac{\lambda_{{}^{40}Ar}}{\lambda} \frac{\lambda_o}{\lambda_{{}^{40}Ar_o}}. \tag{2.12}$$

Note that the quantities ${}^{40}K$ and ${}^{40}K_o$ as I have used them are, in the strictest sense, referring to the number of atoms of $^{40}\mathrm{K}$ that are present in the monitor mineral. These quantities may be re-expressed relative to the total K, K, of the sample by multiplying both sides of the equation by 1, where on the right-hand side we take $1 = K/K$, and the quotient $({}^{40}KK)/({}^{40}K_oK)$ becomes ${}^{40}K_a/{}^{40}K_{ao}$, i.e., the ratio of the "new" isotopic abundance value to the 'old' isotopic abundance value of $^{40}\mathrm{K}$ relative to total K. Hence,

$$J_o = J \frac{{}^{40}K_a}{{}^{40}K_{ao}} \frac{\lambda_{{}^{40}Ar}}{\lambda} \frac{\lambda_o}{\lambda_{{}^{40}Ar_o}}, \tag{2.13}$$

and, in analogy to the final steps we took to arrive at Eq. (2.8), we can substitute Eq. (2.13) into Eq. (2.4) to get an expression for the invariant quantity $({}^{40}Ar/{}^{39}Ar_K)_s$, and then place that result into the general ${}^{40}\mathrm{Ar}/{}^{39}\mathrm{Ar}$ age equation (Eq. (2.1)) to obtain an expression for the 'new' date

$$t = \frac{1}{\lambda}\ \log_e\left[\frac{{}^{40}K_{ao}}{{}^{40}K_a}\frac{\lambda_{{}^{40}Ar_o}}{\lambda_o}\frac{\lambda}{\lambda_{{}^{40}Ar}}(\exp[\lambda_o t_o]-1)+1\right]. \tag{2.14}$$

This is identical to the K-Ar age recalculation equation (Eq. (1.6)), and implies that

$$\frac{{}^{40}K_{ao}}{{}^{40}K_a}\frac{\lambda_{{}^{40}Ar_o}}{\lambda_o}\frac{\lambda}{\lambda_{{}^{40}Ar}} = \frac{\exp[\lambda t_m]-1}{\exp[\lambda_o t_{m_o}]-1}. \tag{2.15}$$

Thus, Eq. (1.6) and Eq. (2.8) are effectively equivalent, and allow legacy K-Ar and ${}^{40}\mathrm{Ar}/{}^{39}\mathrm{Ar}$ dates to be recalculated to adjust for changes in the accepted values for the decay constants of ${}^{40}\mathrm{K}$ and the relative abundances of ${}^{39}\mathrm{K}$, ${}^{40}\mathrm{K}$, and ${}^{41}\mathrm{K}$. Note that, in the strictest sense, this equivalency only applies in the case where changes in the accepted values for the ages of monitor minerals are due solely to updates in the ${}^{40}\mathrm{K}$ decay constants and K isotopic abundances. In the event that the accepted values for monitor mineral ages change by other means (e.g., by improved or additional measurements of a particular monitor), then any ${}^{40}\mathrm{Ar}/{}^{39}\mathrm{Ar}$ dates that rely on those monitors should be recalculated using Eq. (2.8) rather than Eq. (1.6).

2.3 Propagation of Uncertainty

When recalculating ${}^{40}\mathrm{Ar}/{}^{39}\mathrm{Ar}$ dates with Eq. (2.8), there are several sources of uncertainty from: (1) the previously published date, $t_o \pm \sigma_{t_o}$; (2) the decay constants for ${}^{40}\mathrm{K}$: (a) $\lambda_o \pm \sigma_{\lambda_o}$, and (b) $\lambda \pm \sigma_\lambda$; and (3) the monitor mineral ages, (a) $t_{m_o} \pm \sigma_{t_{m_o}}$, and (b) $t_m \pm \sigma_{t_m}$. Of these, only σ_{t_o} is an "internal" source of uncertainty, while σ_{λ_o}, σ_λ, $\sigma_{t_{m_o}}$, and σ_{t_m} are "external" sources of uncertainty. In *ArAR*, the internal uncertainties in the legacy data are always propagated into the recalculated K-Ar dates, and the user has the option of propagating external uncertainties (from either the ${}^{40}\mathrm{K}$ decay constants, monitor mineral ages, or both). In addition, the user may specify whether error propagation should be carried out analytically or by the Monte Carlo method. See the Manual for details on how to select these options.

2.3.1 Analytical Method

Uncertainties are propagated analytically using Eq. (1.7), the general error propagation equation (Taylor, 1997, p. 75). Equation (2.8) is a function with five sources of uncertainty, i.e.,

$t = f(t_o, \lambda_o, \lambda, t_{m_o}, t_m)$, and therefore a recalculated $^{40}Ar/^{39}Ar$ date has the uncertainty

$$\sigma_t = \left[\left(\frac{\partial f}{\partial t_o} \sigma_{t_o} \right)^2 + \left(\frac{\partial f}{\partial \lambda_o} \sigma_{\lambda_o} \right)^2 + \left(\frac{\partial f}{\partial \lambda} \sigma_{\lambda} \right)^2 + \left(\frac{\partial f}{\partial t_{m_o}} \sigma_{t_{m_o}} \right)^2 + \left(\frac{\partial f}{\partial t_m} \sigma_{t_m} \right)^2 \right]^{1/2}. \quad (2.16)$$

The partial differential equations from each of the five terms in Eq. (2.16) are provided below, and even though I have omitted their derivation here, the interested reader is encouraged to consult texts such as Boas (2006) or Rogawski (2008) for details on partial differentiation.

$$\frac{\partial t}{\partial t_o} = \frac{\alpha \lambda_o e^{\lambda_o t_o}}{\lambda(\alpha(e^{\lambda_o t_o} - 1) + 1)}, \quad (2.17a)$$

$$\text{where } \alpha \equiv \frac{e^{\lambda t_m} - 1}{e^{\lambda_o t_{m_o}} - 1}.$$

$$\frac{\partial t}{\partial \lambda_o} = \frac{\eta t_o e^{\lambda_o t_o} - t_{m_o} e^{\lambda_o t_{m_o}} \left(e^{\lambda t} - 1 \right)}{\lambda e^{\lambda t} (e^{\lambda_o t_{m_o}} - 1)}, \quad (2.17b)$$

$$\text{where } \eta \equiv e^{\lambda t_m} - 1.$$

$$\frac{\partial t}{\partial \lambda} = \frac{\eta' t_m e^{\lambda t_m} - t e^{\lambda t}}{\lambda e^{\lambda t}}, \quad (2.17c)$$

$$\text{where } \eta' \equiv \frac{e^{\lambda_o t_o} - 1}{e^{\lambda_o t_{m_o}} - 1}.$$

$$\frac{\partial t}{\partial t_{m_o}} = \frac{-\gamma \lambda_o e^{\lambda_o t_{m_o}}}{\lambda(\gamma + e^{\lambda_o t_{m_o}} - 1)(e^{\lambda_o t_{m_o}} - 1)}, \quad (2.17d)$$

$$\text{where } \gamma \equiv (e^{\lambda t_m} - 1)(e^{\lambda_o t_o} - 1).$$

$$\frac{\partial t}{\partial t_m} = \frac{\gamma' e^{\lambda t_m}}{\gamma'(e^{\lambda t_m} - 1) + 1}, \quad (2.17e)$$

$$\text{where } \gamma' \equiv \frac{e^{\lambda_o t_o} - 1}{e^{\lambda_o t_{m_o}} - 1}.$$

In *ArAR*, Eqs. (2.17) are computed for each recalculated $^{40}Ar/^{39}Ar$ date and the results are substituted into Eq. (2.16). If any external sources of uncertainty are excluded by the user, then the corresponding values (i.e., σ_{λ_o}, σ_{λ}, $\sigma_{t_{m_o}}$, and/or σ_{t_m}) are set to zero. This effectively reduces the number of terms that contribute to the uncertainty of the recalculated $^{40}Ar/^{39}Ar$ date (the uncertainty in t_o is always propagated).

2.3.2 Monte Carlo Method

In abstract, the Monte Carlo method relies on the repeated sampling of large populations of values representing distinct quantities to compute a population of results using some predefined mathematical combination of the sample values. Inferences can then be made on the population of results using descriptive statistics.

Because Eq. (2.8) is a function of five variables, synthetic populations are generated for each variable (t_o, λ_o, λ, t_{m_o}, and t_m). Each synthetic population contains pseudo-random numbers that are normally distributed[4] about a central value (e.g., t_o) with standard deviation equal to the uncertainty in the central value (e.g., σ_{t_o}). Each synthetic population has the same size (i.e., the number of values in each population is the same), which can be specified in the main *ArAR* GUI (see the Manual for details on how to edit the size of the synthetic populations). If the uncertainty for a particular variable is set to zero (e.g., if $\sigma_\lambda = 0$ because external uncertainties from the ^{40}K decay constants are not being propagated), then every member of the synthetic population for that variable will equal the mean value of the variable (e.g., all values in the synthetic population for λ will be identically equal to λ).

Once the five synthetic populations are generated for t_o, λ_o, λ, t_{m_o}, and t_m (with standard deviations given by σ_{t_o}, σ_{λ_o}, σ_λ, σt_{m_o}, and σ_{t_m}, respectively), a synthetic 'results' population of recalculated ^{40}Ar/^{39}Ar dates is generated in the following way: (1) a single value is randomly drawn from each of the five source populations[5]; (2) a synthetic recalculated ^{40}Ar/^{39}Ar date is computed using Eq. (2.8) and is stored in the results population; (3) steps 1 and 2 are repeated until the results population has the size specified in the main *ArAR* GUI. The results population is normally distributed about a central value[6], and the uncertainty can be inferred simply by calculating the sample standard deviation:

$$\sigma_t = \sqrt{\frac{1}{N-1}\sum_{i=1}^{N}(t_i - \bar{t})^2},$$

where N is the size of the results population, the subscript i represents an individual value in the population, and

$$\bar{t} \equiv \frac{1}{N}\sum_{i=1}^{N} t_i$$

is the mean of the results population. The value of σ_t is returned when errors are propagated by

[4] The values in each synthetic population are drawn from a Gaussian, or 'normal,' limiting distribution.

[5] Note: every value in the synthetic source populations has an equal probability of being drawn, and the values are not removed permanently.

[6] The mean of the results population will be close to the analytically recalculated ^{40}Ar/^{39}Ar date. As the population size approaches infinity, the mean value of the results population will converge on the analytical result. Note, however, that *ArAR always* returns the analytical result for the recalculated ^{40}Ar/^{39}Ar date, and only uses the synthetic results population to infer an uncertainty in the recalculated date.

the Monte Carlo method.

2.4 Implementation Notes

If $^{40}Ar/^{39}Ar$ dates are entered in units of ka or Ga, they are first converted to units of Ma for calculations. The ^{40}K decay constants must be entered with units of a^{-1}, and they are converted to units of Ma^{-1} for calculations. After the $^{40}Ar/^{39}Ar$ dates have been recalculated, they are converted back to their original units (i.e., ka or Ga).

If the total ^{40}K decay constant, e.g., λ, is determined automatically from the partial decay constants, e.g., $\lambda_{^{40}Ar}$ and λ_β, then the uncertainty, e.g., σ_λ, is determined by analytical error propagation (see Eq. (1.7)).

3 Intercalibration with Multiple Coirradiated Standards

3.1 Intercalibration Methods

A K-bearing mineral may be intercalibrated relative to a 'primary' standard and an arbitrary number of secondary standards with known K-Ar or $^{40}Ar/^{39}Ar$ ages using the methods of Karner and Renne (1998) and Renne et al. (1998). For convenience, we reproduce Eqs. 1–3 (Eqs. (3.1) a–c) and Eq. 5 (Eq. (3.2)) from Renne et al. (1998) below. Note that these equations only apply for samples that have been coirradiated, i.e., all the grains were simultaneously irradiated in the same palette. The intercalibrated age, t_u, of an 'unknown' sample relative to a 'primary' standard with a known K-Ar age[7] and zero or more secondary standards is given by:

$$t_u = \frac{1}{\lambda}\log_e\left[\frac{\lambda}{\lambda_{^{40}Ar}}\kappa\prod_{i=0}^{n-1}R_i^{i+1}+1\right], \tag{3.1a}$$

where

$$\kappa \equiv \left(\frac{^{40}Ar^*}{^{40}K}\right)_{i=0} \tag{3.1b}$$

is known for the 'primary' standard ($i=0$), and

$$R_i^{i+1} \equiv \frac{F_{i+1}}{F_i} = \frac{\left(\frac{^{40}Ar^*}{^{39}Ar_K}\right)_{i+1}}{\left(\frac{^{40}Ar^*}{^{39}Ar_K}\right)_i} = \frac{\exp[\lambda t_{i+1}]-1}{\exp[\lambda t_i]-1}. \tag{3.1c}$$

[7] In a more fundamental sense, the 'primary' standard must have a known $^{40}Ar^*/K$ ratio, where K is the total potassium concentration of the sample. The $^{40}Ar^*/^{40}K$ ratio and K-Ar age of the standard are then determined by choosing sets of values for the isotopic abundances of K and the ^{40}K decay constants, respectively.

The variable n is the total number of 'primary' and 'secondary' standards used to intercalibrate the unknown sample. For $i = 0$, $R_0^1 = F_1/F_0$ represents the ratio of the F value of the first 'secondary' standard to that of the 'primary' standard. For values of i in the range $1 \leq i < n-1$, R_i^{i+1} represents the ratio of F values between successive 'secondary' standards. For $i = n-1$, R_{n-1}^n is the ratio of the F value for the unknown sample to that of the last 'secondary' standard.

If the age of the 'primary' standard, t_0, was determined by some other means, the equivalent expression to Eq. (3.1a) is:

$$t_u = \frac{1}{\lambda} \log_e \left[(\exp[\lambda t_0] - 1) \prod_{i=0}^{n-1} R_i^{i+1} + 1 \right], \tag{3.2}$$

where R_i^{i+1} is the same as Eq. (3.1c). Note that Eqs. (3.1) a-c and Eq. (3.2) all use a single value for the total ^{40}K decay constant λ, and that calculating Eq. (3.1b) requires an assumption about the relative isotopic abundances of K. Suppose that published isotopic data exist for coirradiated standards but the accepted values for λ (i.e., $\lambda_{^{40}Ar}$ and λ_β) and/or $^{40}K_a$ have changed. A 'new' value for κ (Eq. (3.1b)) can be determined using

$$\kappa = \kappa_o \frac{^{40}K_a}{^{40}K_{ao}},$$

where κ_o is the originally published value, and then Eqs. (3.1) a–c can be used to determine a new intercalibrated age using κ and the new decay constants. Finally, note that, for $n = 1$ and $R_i^{i+1} = (\exp[\lambda t_{i+1}] - 1)/(\exp[\lambda t_i] - 1)$, Eq. (3.2) reduces to a form identical to Eq. (2.8). The only difference in Eq. (2.8) is that we have allowed the ^{40}K decay constants and monitor mineral age in the R factor to represent the 'old' values used to calculate the legacy ^{40}Ar/^{39}Ar date, t_o.

When there are number of replicate analyses for a single standard, S, that is being intercalibrated against a primary standard, P, using Eqs. (3.1) a–c, researchers have commonly calculated some form of a mean F_S value from the replicate $F_{S_i} = (^{40}\mathrm{Ar}^*/^{39}\mathrm{Ar}_\mathrm{K})_{S_i}$ ratios. Some have calculated a simple arithmetic mean and used either the sample standard deviation (σ_{F_S}, e.g., Nomade et al., 2005) or the standard deviation of the mean ($\sigma_{F_S}/\sqrt{N}$, e.g., Renne et al., 1998; Jourdan et al., 2006) as an estimate of the uncertainty, while others calculated the inverse-variance weighted mean and standard deviation of the mean (e.g., Spell and McDougall, 2003). Once a mean F_S value is determined, a single $R_P^S = F_S/F_P$ value can be determined and Eqs. (3.1) a–c may be used (with $n = 1$) to determine an intercalibrated age of the standard S. All three methods for determining the mean F value and its associated uncertainty for a single standard are available as supplementary intercalibration options in *ArAR*. See section 3.2 for details on the propagation of uncertainties for multiple intercalibration, and see sections 3.5 and 3.6 for details on supplemental intercalibration calculations.

3.2 Propagation of Uncertainty

When intercalibrating a sample to multiple 'primary' and 'secondary' standards using Eqs. (3.1) a–c, there are several sources of uncertainty from: (1) the ^{40}K decay constants: (a) $\lambda_{^{40}Ar} \pm \sigma_{\lambda_{^{40}Ar}}$, and (b) $\lambda_\beta \pm \sigma_{\lambda_\beta}$; (2) the value of κ (Eq. (3.1b)) for the 'primary' standard: $\kappa \pm \sigma_\kappa$; and (3) the value(s) of R_i^{i+1} (Eq. (3.1c)) between the various standards and the unknown sample: $R_i^{i+1} \pm \sigma_{R_i^{i+1}}$. When intercalibrating a sample using Eq. (3.2), the sources of uncertainty are: (1) the ^{40}K total decay constant: $\lambda \pm \sigma_\lambda$; (2) the age of the 'primary' standard: $t_0 \pm \sigma_{t_0}$; and (3) the value(s) of R_i^{i+1} (as above). Of these, σ_κ, σ_{t_0}, and $\sigma_{R_i^{i+1}}$ are 'internal' sources of uncertainty, while σ_λ, $\sigma_{\lambda_{^{40}Ar}}$, and σ_{λ_β} are 'external' sources of uncertainty. In *ArAR* , the internal uncertainties in the legacy data are always propagated into the intercalibrated standard age, and the user has the option of propagating external uncertainties (from the ^{40}K decay constants). In addition, the user may specify whether error propagation should be carried out analytically or by the Monte Carlo method.

3.3 Analytical Approach

Karner and Renne (1998) and Renne et al. (1998) provided analytical equations for the propagation of uncertainties through Eqs. (3.1) a–c and Eq. (3.2). These equations are reproduced below term by term, and were originally derived using the same general error propagation equation for independent and random quantities (Eq. (1.7)) that we have applied to Eq. (1.6) and Eq. (2.8).

Equation (3.1a) is a function with four or more sources of uncertainty, depending on how many standards are used in the intercalibration. For example, if an unknown sample is intercalibrated relative to a single primary standard (i.e., $n = 1$), then $t_u = f(\lambda_{^{40}Ar}, \lambda_\beta, \kappa, R_0^1)$. If an unknown sample is instead intercalibrated relative to a primary monitor and two secondary standards (i.e., $n = 3$), then $t_u = f(\lambda_{^{40}Ar}, \lambda_\beta, \kappa, R_0^1, R_1^2, R_2^3)$. In general, an ^{40}Ar/^{39}Ar date intercalibrated using Eq. (3.1a) has the uncertainty

$$\sigma_{t_u} = \left[\left(\frac{\partial t}{\partial \lambda_{^{40}Ar}} \sigma_{\lambda_{^{40}Ar}} \right)^2 + \left(\frac{\partial t}{\partial \lambda_\beta} \sigma_{\lambda_\beta} \right)^2 + \left(\frac{\partial t}{\partial \kappa} \sigma_\kappa \right)^2 + \sum_{j=0}^{n-1} \left(\frac{\partial t}{\partial R_j^{j+1}} \sigma_{R_j^{j+1}} \right)^2 \right]^{1/2}. \tag{3.3}$$

The partial differential equations from each of the terms in Eq. (3.3) are provided below (Karner and Renne, 1998; Renne et al., 1998).

$$\frac{\partial t_u}{\partial \lambda_{^{40}Ar}} = -\frac{1}{\lambda} \left(t_u + \frac{\lambda_\beta \kappa \prod_{i=0}^{n-1} R_i^{i+1}}{\lambda_{^{40}Ar}^2 e^{\lambda t_u}} \right), \tag{3.4a}$$

$$\frac{\partial t_u}{\partial \lambda_\beta} = \frac{1}{\lambda}\left(-t_u + \frac{\kappa\prod_{i=0}^{n-1} R_i^{i+1}}{\lambda_{^{40}Ar} + \lambda\kappa\prod_{i=0}^{n-1} R_i^{i+1}}\right), \tag{3.4b}$$

$$\frac{\partial t_u}{\partial \kappa} = \frac{\prod_{i=0}^{n-1} R_i^{i+1}}{\lambda_{^{40}Ar} + \lambda\kappa\prod_{i=0}^{n-1} R_i^{i+1}}, \tag{3.4c}$$

$$\frac{\partial t_u}{\partial R_j^{j+1}} = \frac{\kappa\prod_{i=0}^{n-1} R_i^{i+1}}{R_j^{j+1}\left(\lambda_{^{40}Ar} + \lambda\kappa\prod_{i=0}^{n-1} R_i^{i+1}\right)}. \tag{3.4d}$$

Note the use of two separate indexes, i and j, in Eq. (3.4d).

Equation (3.2) is a function with three or more sources of uncertainty, again depending on the number of standards that are used in the intercalibration, i.e., $t_u = f(\lambda, t_0, R_0^1, R_1^2, \ldots, R_i^{i+1})$ for $i < n$. In general, an $^{40}Ar/^{39}Ar$ date intercalibrated using Eq. (3.2) has the uncertainty

$$\sigma_{t_u} = \left[\left(\frac{\partial t}{\partial \lambda}\sigma_\lambda\right)^2 + \left(\frac{\partial t}{\partial t_0}\sigma_{t_0}\right)^2 + \sum_{j=0}^{n-1}\left(\frac{\partial t}{\partial R_j^{j+1}}\sigma_{R_j^{j+1}}\right)^2\right]^{1/2}. \tag{3.5}$$

The partial differential equations from each of the terms in Eq. (3.5) are provided below (Renne et al., 1998).

$$\frac{\partial t_u}{\partial \lambda} = \frac{1}{\lambda}\left(-t_u + t_0 e^{\lambda(t_0 - t_u)}\prod_{i=0}^{n-1} R_i^{i+1}\right), \tag{3.6a}$$

$$\frac{\partial t_u}{\partial t_0} = e^{\lambda(t_0 - t_u)}\prod_{i=0}^{n-1} R_i^{i+1}, \tag{3.6b}$$

$$\frac{\partial t_u}{\partial R_j^{j+1}} = \frac{(e^{\lambda t_0} - 1)\prod_{i=0}^{n-1} R_i^{i+1}}{\lambda e^{\lambda t_u} R_j^{j+1}}. \tag{3.6c}$$

Note the use of two separate indexes, i and j, in Eq. (3.6c).

In *ArAR* , Eqs. (3.4) are computed and substituted into Eq. (3.3), or Eqs. (3.6) are computed and substituted into Eq. (3.5), depending on the intercalibration algorithm selected by the user. If any external sources of uncertainty are excluded by the user, then the corresponding values ($\sigma_{\lambda_{^{40}Ar}}$, and σ_{λ_β} in Eq. (3.3); σ_λ in Eq. (3.5)) are set to zero. This effectively reduces the number of terms

that contribute to the uncertainty of the intercalibrated $^{40}Ar/^{39}Ar$ date (the uncertainties in σ_κ, σ_{t_0}, and R_j^{j+1} are always propagated).

The uncertainty in R_j^{j+1} can be determined using the general error propagation equation, Eq. (1.7). In case (A), where

$$R_j^{j+1} = \frac{\left(\frac{^{40}Ar^*}{^{39}Ar_K}\right)_{j+1}}{\left(\frac{^{40}Ar^*}{^{39}Ar_K}\right)_j} = \frac{F_{j+1}}{F_j}, \tag{3.7}$$

the uncertainty in the R_j^{j+1} is given by

$$\sigma_{R_j^{j+1}} = R_j^{j+1}\left[\left(\frac{\sigma_{F_{j+1}}}{F_{j+1}}\right)^2 + \left(\frac{\sigma_{F_j}}{F_j}\right)^2\right]^{1/2}. \tag{3.8}$$

In case (B), where

$$R_j^{j+1} = \frac{\exp[\lambda t_{j+1}] - 1}{\exp[\lambda t_j] - 1} = \frac{F_{j+1}}{F_j}, \tag{3.9}$$

the uncertainty in the R_j^{j+1} is given by

$$\sigma_{R_j^{j+1}} = \left[\left(\frac{\partial R_j^{j+1}}{\partial \lambda}\sigma_\lambda\right)^2 + \left(\frac{\partial R_j^{j+1}}{\partial t_{j+1}}\sigma_{t_{j+1}}\right)^2 + \left(\frac{\partial R_j^{j+1}}{\partial t_j}\sigma_{t_j}\right)^2\right]^{1/2}, \tag{3.10}$$

where the partial differential equations are

$$\frac{\partial R_j^{j+1}}{\partial \lambda} = \frac{t_{j+1}e^{\lambda t_{j+1}} - t_j e^{\lambda t_j} R_j^{j+1}}{e^{\lambda t_j} - 1}, \tag{3.11a}$$

$$\frac{\partial R_j^{j+1}}{\partial t_{j+1}} = \frac{\lambda e^{\lambda t_{j+1}}}{e^{\lambda t_j} - 1}, \tag{3.11b}$$

$$\frac{\partial R_j^{j+1}}{\partial t_j} = -\frac{\lambda e^{\lambda t_j} R_j^{j+1}}{e^{\lambda t_j} - 1}. \tag{3.11c}$$

3.4 Monte Carlo Approach

When a sample is intercalibrated relative to a primary standard and one or more secondary standards, the uncertainties in each ratio R_i^{i+1} (for $0 \leq i < n$) are determined first. In case (A), where Eq. (3.7) applies, synthetic populations of pseudo-random numbers are generated for the

quantities $F_i = ({}^{40}Ar^*/{}^{39}Ar_K)_i$ and $F_{i+1} = ({}^{40}Ar^*/{}^{39}Ar_K)_{i+1}$, which are normally distributed[8] about a central value (e.g., F_i) with standard deviation equal to the uncertainty in the central value (e.g., σ_{F_i}). Each synthetic population has the same size (i.e., the number of values in each population is the same), which can be specified in the *ArAR* Multiple Intercalibration Tool window. Next, a synthetic 'results' population of R_i^{i+1} values, where $(R_i^{i+1})_j = (F_{i+1})_j/(F_i)_j$, is generated in the following way: (1) a single value (with index j) is randomly drawn from each of the source populations[9]; (2) a synthetic $(R_i^{i+1})_j$ value is computed using Eq. (3.7) and is stored in the results population; (3) steps 1 and 2 are repeated until the results population has the size specified in the *ArAR* Multiple Intercalibration Tool window. The results population is normally distributed about a central value[10], and the uncertainty can be inferred simply by calculating the sample standard deviation:

$$\sigma_{R_i^{i+1}} = \sqrt{\frac{1}{N-1}\sum_{j=1}^{N}\left(\left(R_i^{i+1}\right)_j - \overline{R_i^{i+1}}\right)^2},$$

where N is the size of the results population, the subscript i represents an individual value in the population, and

$$\overline{R_i^{i+1}} \equiv \frac{1}{N}\sum_{j=1}^{N}\left(R_i^{i+1}\right)_j$$

is the mean of the results population. The uncertainties for each R value, $\sigma_{R_i^{i+1}}$, are reported for convenience, and the synthetic populations for each R value, R_i^{i+1}, are used again in later calculations when errors are propagated by the Monte Carlo method for multiple intercalibration.

In case (B), where Eq. (3.9) applies, synthetic populations of pseudo-random numbers are generated for the quantities λ, t_i, and t_{i+1}, which are normally distributed[11] about a central value (e.g., λ) with standard deviation equal to the uncertainty in the central value (e.g., σ_λ). Each synthetic population has the same size (i.e., the number of values in each population is the same), which can be specified in the *ArAR* Multiple Intercalibration Tool window. Next, intermediate synthetic populations are generated (separately) for the quantities F_i and F_{i+1} in the following general way: (1) a single value (with index j) is randomly drawn from each of the appropriate source populations[12]; (2) a synthetic $(F_i)_j = (\exp[\lambda(t_i)_j] - 1)$ or $(F_{i+1})_j = (\exp[\lambda(t_{i+1})_j] - 1)$ value

[8] The values in each synthetic population are drawn from a Gaussian, or 'normal,' limiting distribution.

[9] Note: every value in the synthetic source populations has an equal probability of being drawn, and the values are not removed permanently.

[10] The mean of the results population will be close to the analytically determined R value, R_i^{i+1}. As the population size approaches infinity, the mean value of the results population will converge on the analytical result. Note, however, that *ArAR always* returns the analytical result for the R_i^{i+1}, and only uses the synthetic results population to infer an uncertainty, $\sigma_{R_i^{i+1}}$.

[11] The values in each synthetic population are drawn from a Gaussian, or 'normal,' limiting distribution.

[12] Note: every value in the synthetic source populations has an equal probability of being drawn, and the values are not removed permanently.

is computed and is stored in the appropriate intermediate population; (3) steps 1 and 2 are repeated until the intermediate populations have the size specified in the *ArAR* Multiple Intercalibration Tool window. Next, a synthetic 'results' population of R_i^{i+1} values is generated in the following way: (1) a single value (with index j) is randomly drawn from each of the source populations (for F_i and F_{i+1})[13]; (2) a synthetic value is computed by taking the ratio $(R_i^{i+1})_j = (F_{i+1})_j/(F_i)_j$, consistent with Eq. (3.9), and is stored in the results population; (3) steps 1 and 2 are repeated until the results population has the size specified in the *ArAR* Multiple Intercalibration Tool window. The results population is normally distributed about a central value[14], and the uncertainty can be inferred simply by calculating the sample standard deviation:

$$\sigma_{R_i^{i+1}} = \sqrt{\frac{1}{N-1}\sum_{j=1}^{N}\left(\left(R_i^{i+1}\right)_j - \overline{R_i^{i+1}}\right)^2},$$

where N is the size of the results population, the subscript i represents an individual value in the population, and

$$\overline{R_i^{i+1}} \equiv \frac{1}{N}\sum_{j=1}^{N}\left(R_i^{i+1}\right)_j$$

is the mean of the results population. The uncertainties for each R value, $\sigma_{R_i^{i+1}}$, are reported for convenience, and the synthetic populations for each R value, R_i^{i+1}, are used again in later calculations when errors are propagated by the Monte Carlo method for multiple intercalibration.

Once synthetic populations have been generated for each R_i^{i+1} (for $0 \leq i < n$), synthetic populations are also generated for each additional quantity in either Eqs. (3.1) (i.e., $\lambda_{^{40}Ar}$, λ, κ) or Eq. (3.2) (i.e., λ, t_0), depending on the algorithm selected by the end user. The total number of synthetic populations depends on the total number of standards (n) that are being used to calibrate the unknown sample. Each synthetic population contains pseudo-random numbers that are normally distributed about a central value (e.g., λ) with standard deviation equal to the uncertainty in the central value (e.g., σ_λ). Each synthetic population has the same size (i.e., the number of values in each population is the same), which can be specified in the *ArAR* Multiple Intercalibration Tool window. If the uncertainty for a particular variable is set to zero (e.g., if $\sigma_\lambda = 0$ because external uncertainties from the ^{40}K decay constants are not being propagated), then every member of the synthetic population for that variable will equal the mean value of the variable (e.g., all values in

[13] Note: every value in the synthetic source populations has an equal probability of being drawn, and the values are not removed permanently.

[14] The mean of the results population will be close to the analytically determined R value, R_i^{i+1}. As the population size approaches infinity, the mean value of the results population will converge on the analytical result. Note, however, that *ArAR always* returns the analytical result for the R_i^{i+1}, and only uses the synthetic results population to infer an uncertainty, $\sigma_{R_i^{i+1}}$.

the synthetic population for λ will be identically equal to λ).

Once the synthetic synthetic populations are generated for the appropriate quantities in Eqs. (3.1) or Eq. (3.2), a synthetic 'results' population of intercalibrated monitor dates is generated in the following way: (1) a single value is randomly drawn from each of the source populations[15]; (2) a synthetic intercalibrated $^{40}Ar/^{39}Ar$ date is computed using either Eqs. (3.1) or Eq. (3.2) and is stored in the results population; (3) steps 1 and 2 are repeated until the results population has the size specified in the *ArAR* Multiple Intercalibration Tool window. The results population is normally distributed about a central value[16], and the uncertainty can be inferred simply by calculating the sample standard deviation:

$$\sigma_{t_u} = \sqrt{\frac{1}{N-1}\sum_{i=1}^{N}(t_{u_i} - \overline{t_u})^2},$$

where N is the size of the results population, the subscript i represents an individual value in the population, and

$$\overline{t_u} \equiv \frac{1}{N}\sum_{i=1}^{N} t_{u_i}$$

is the mean of the results population. The value of σ_{t_u} is returned when errors are propagated by the Monte Carlo method for multiple intercalibration.

3.5 Supplemental Intercalibrations Using the Mean F Value

For a single standard, S, replicate $F_{S_i} = (^{40}Ar^*/^{39}Ar_K)_{S_i}$ values may be entered in the *ArAR* Multiple Intercalibration Tool Window. The user may choose to perform a supplemental intercalibration using a mean F_S value to determine a single $R_P^S = F_S/F_P$ value relative to the primary standard, P. Either an arithmetic mean or an inverse-variance weighted mean F_S may be determined. The arithmetic mean is calculated as

$$\overline{F_S} = \frac{1}{N}\sum_{i=1}^{N} F_{S_i}, \tag{3.12}$$

[15]Note: every value in the synthetic source populations has an equal probability of being drawn, and the values are not removed permanently.

[16]The mean of the results population will be close to the analytically intercalibrated $^{40}Ar/^{39}Ar$ date. As the population size approaches infinity, the mean value of the results population will converge on the analytical result. Note, however, that *ArAR always* returns the analytical result for the intercalibrated $^{40}Ar/^{39}Ar$ date, and only uses the synthetic results population to infer an uncertainty in the intercalibrated date.

where N is the number of replicates, and the uncertainty can either be determined as the sample standard deviation

$$\sigma_{F_S} = \sqrt{\frac{1}{N-1}\sum_{i=1}^{N}\left(F_{S_i} - \overline{F_S}\right)^2} \tag{3.13}$$

or as the standard deviation of the mean

$$\sigma_{\overline{F_S}} = \sigma_{F_S}/\sqrt{N}. \tag{3.14}$$

The inverse-variance weighted mean is calculated as

$$\left(\overline{F_S}\right)_w = \frac{\sum_{i=1}^{N}\omega_i F_{S_i}}{\sum_{i=1}^{N}\omega_i}, \tag{3.15}$$

where $\omega_i \equiv 1/\sigma^2_{F_{S_i}}$, and the standard deviation of the mean is determined as

$$\left(\sigma_{\overline{F_S}}\right)_w = \frac{1}{\sqrt{\sum_{i=1}^{N}\omega_i}}. \tag{3.16}$$

Once a mean F_S value, $\mathfrak{F}_{\mathfrak{S}}$, is determined, the MSWD, also known as the reduced chi-squared statistic, is calculated as follows:

$$\text{MSWD} \equiv \frac{1}{N-1}\sum_{i=1}^{N}\frac{(F_{S_i} - \mathfrak{F}_{\mathfrak{S}})^2}{\sigma^2_{F_{S_i}}}. \tag{3.17}$$

The MSWD will have a value near unity if the value of $\mathfrak{F}_{\mathfrak{S}}$ fits the population of F_{S_i} values well. If $\text{MSWD} > 1 + 2\cdot\sqrt{2/(N-1)}$, then it is possible that the uncertainties $\sigma_{F_{S_i}}$ were underestimated and do not adequately account for the scatter of the F_{S_i} values about the mean, $\mathfrak{F}_{\mathfrak{S}}$. If the user feels that this is indeed the case, they have the option to have the *ArAR* Multiple Intercalibration Tool expand the uncertainty in $\mathfrak{F}_{\mathfrak{S}}$, i.e., $\sigma_{\mathfrak{F}_{\mathfrak{S}}}$, by the $\sqrt{\text{MSWD}}$. This expansion inflates the $\sigma_{F_{S_i}}$ values such that the MSWD becomes identically equal to unity, and therefore serves as a method to account for excess dispersion in the F_{S_i} values. Note: this should not necessarily be used mechanistically; it is important that the researcher critically evaluate whether this error expansion technique is warranted in each case where $\text{MSWD} > 1 + 2\cdot\sqrt{2/(N-1)}$. For more information about the MSWD, the interested reader is referred to Wendt and Carl (1991).

Once the mean F_S value, $\mathfrak{F}_{\mathfrak{S}}$, and its associated uncertainty, $\sigma_{\mathfrak{F}_{\mathfrak{S}}}$, are determined, a single

intercalibration factor is calculated using

$$R_P^S = \mathfrak{F}_{\mathfrak{S}}/F_P, \tag{3.18}$$

and the associated uncertainty is calculated using

$$\sigma_{R_P^S} = R_P^S \left[\left(\frac{\sigma_{\mathfrak{F}_{\mathfrak{S}}}}{\mathfrak{F}_{\mathfrak{S}}} \right)^2 + \left(\frac{\sigma_{F_P}}{F_P} \right)^2 \right]. \tag{3.19}$$

Finally, Eqs. (3.1) a–c are used (with $n = 1$) to determine an intercalibrated age of the standard S. Error propagation occurs as described in sections 3.3 and 3.4.

3.6 Calculated Values of κ and t_0 for the Primary Monitor

By default, the user must supply the value of either κ or t_0 for the 'primary' standard when using Eqs. (3.1) a-c or Eq. (3.2), respectively, to intercalibrate an unknown in the *ArAR* Multiple Intercalibration Tool. However, the user may optionally have *ArAR* determine: (1) κ from t_0 before employing the result in Eqs. (3.1) a-c, or (2) t_0 from κ before employing the result in Eq. (3.2). The following sections describe these calculations and the associated propagation of uncertainties.

3.6.1 Calculating κ from t_0

The K-Ar age of the 'primary' standard is given by

$$t_0 = \frac{1}{\lambda} \log_e \left[\frac{\lambda}{\lambda_{^{40}Ar}} \kappa + 1 \right], \tag{3.20}$$

where $\kappa \equiv {}^{40}Ar^*/{}^{40}K$. Solving for κ, we obtain

$$\kappa = \frac{\lambda_{^{40}Ar}}{\lambda} \left(e^{\lambda t_0} - 1 \right). \tag{3.21}$$

To calculate the uncertainty, σ_κ, it is useful to rewrite Eq. (3.21) as

$$\kappa = \frac{\lambda_{^{40}Ar}}{\lambda_{^{40}Ar} + \lambda_\beta} \left(e^{(\lambda_{^{40}Ar} + \lambda_\beta) t_0} - 1 \right), \tag{3.22}$$

since $\lambda \equiv \lambda_{^{40}Ar} + \lambda_\beta$. Then, applying the general error propagation equation (Eq. (1.7)), the uncertainty in κ is given by

$$\sigma_\kappa = \left[\left(\frac{\partial \kappa}{\partial \lambda_{^{40}Ar}} \sigma_{\lambda_{^{40}Ar}} \right)^2 + \left(\frac{\partial \kappa}{\partial \lambda_\beta} \sigma_{\lambda_\beta} \right)^2 + \left(\frac{\partial \kappa}{\partial t_0} \sigma_{t_0} \right)^2 \right]^{1/2}, \tag{3.23}$$

where the partial differential equations are

$$\frac{\partial \kappa}{\partial \lambda_{^{40}Ar}} = \frac{(\lambda_\beta + \lambda_{^{40}Ar}\lambda t_0)e^{\lambda t_0} - \lambda_\beta}{\lambda^2}, \tag{3.24a}$$

$$\frac{\partial \kappa}{\partial \lambda_\beta} = \frac{\lambda_{^{40}Ar}}{\lambda^2}\left[1 + (\lambda t_0 - 1)e^{\lambda t_0}\right], \tag{3.24b}$$

$$\frac{\partial \kappa}{\partial t_0} = \lambda_{^{40}Ar} e^{\lambda t_0}. \tag{3.24c}$$

In *ArAR*, Eqs. (3.24) are computed and the results are substituted into Eq. (3.23). If any external sources of uncertainty are excluded by the user, then the corresponding values (i.e., $\sigma_{\lambda_{^{40}Ar}}$ and σ_{λ_β}) are set to zero. This effectively reduces the number of terms that contribute to the uncertainty of κ (the uncertainty in t_0 is always propagated).

3.6.2 Calculating t_0 from κ

To determine the value of t_0 from κ, we simply employ Eq. (3.20). To calculate the uncertainty, σ_{t_0}, it is useful to rewrite Eq. (3.20) as

$$t_0 = \frac{1}{\lambda_{^{40}Ar} + \lambda_\beta} \log_e \left[\frac{\lambda_{^{40}Ar} + \lambda_\beta}{\lambda_{^{40}Ar}}\kappa + 1\right], \tag{3.25}$$

since $\lambda \equiv \lambda_{^{40}Ar} + \lambda_\beta$. Then, applying the general error propagation equation (Eq. (1.7)), the uncertainty in t_0 is given by

$$\sigma_{t_0} = \left[\left(\frac{\partial t_0}{\partial \lambda_{^{40}Ar}}\sigma_{\lambda_{^{40}Ar}}\right)^2 + \left(\frac{\partial t_0}{\partial \lambda_\beta}\sigma_{\lambda_\beta}\right)^2 + \left(\frac{\partial t_0}{\partial \kappa}\sigma_\kappa\right)^2\right]^{1/2}, \tag{3.26}$$

where the partial differential equations are

$$\frac{\partial t_0}{\partial \lambda_{^{40}Ar}} = -\frac{1}{\lambda}\left(\frac{\lambda_\beta \kappa}{\lambda_{^{40}Ar}\lambda\kappa + \lambda_{^{40}Ar}} + t_0\right), \tag{3.27a}$$

$$\frac{\partial t_0}{\partial \lambda_\beta} = \frac{1}{\lambda}\left(\frac{\kappa}{\lambda\kappa + \lambda_{^{40}Ar}} - t_0\right), \tag{3.27b}$$

$$\frac{\partial t_0}{\partial \kappa} = \frac{1}{\lambda\kappa + \lambda_{^{40}Ar}}. \tag{3.27c}$$

In *ArAR*, Eqs. (3.27) are computed and the results are substituted into Eq. (3.26). If any external sources of uncertainty are excluded by the user, then the corresponding values (i.e., $\sigma_{\lambda_{^{40}Ar}}$ and σ_{λ_β}) are set to zero. This effectively reduces the number of terms that contribute to the uncertainty of t_0 (the uncertainty in κ is always propagated).

Appendix

A Derivation of the K-Ar and $^{40}Ar/^{39}Ar$ Age Equations

A.1 Basic Theory

Unstable nuclides spontaneously transform to other nuclides, either stable or unstable, by the emission of energy in the form of particles or photons. This phenomenon is called radioactive decay, and while any given decay event occurs randomly, a large population of unstable "parent" nuclides will decay over time to one or more "daughter" nuclides at a rate that is proportional to the number of parent nuclides remaining. Thus, the time-rate of change in the number of parent nuclides, dn_p/dt, is described by

$$-\frac{dn_p}{dt} \propto n_p, \tag{A.1}$$

where n_p is the number of parent nuclides present at any given time, and the negative sign signifies that the number of parent nuclides decreases over time. The proportionality expressed by Eq. (A.1) is transformed into an equality by the introduction of a proportionality constant, λ_p, called the decay constant:

$$-\frac{dn_p}{dt} = \lambda_p n_p. \tag{A.2}$$

The value of λ_p is characteristic of each parent radionuclide, and describes the probability that a parent nuclide will decay over a given time interval.

Rearranging Eq. (A.2) and preparing to integrate both sides, we obtain

$$\int dn_p \frac{1}{n_p} = -\int dt\ \lambda_p. \tag{A.3}$$

Assuming that λ_p is constant in time, we may integrate both sides to get

$$\log_e[n_p] = -\lambda_p t + c_1, \tag{A.4}$$

where $\log_e[n_p]$ is the natural logarithm of n_p, and c_1 is a constant of integration. Exponentiating

both sides, we get

$$n_p = \exp[-\lambda_p t + c_1] = \exp[c_1]\exp[-\lambda_p t] = c_2 \exp[-\lambda_p t]. \tag{A.5}$$

To determine c_2, we impose the initial condition that $n_p(t=0) = n_{p0}$. Hence, $c_2 = n_{p0}$, and

$$n_p(t) = n_{p0}\exp[-\lambda_p t]. \tag{A.6}$$

The halflife, $t_{1/2}$, of a radionuclide is defined as the amount of time that is required for half of the initial parent population of a radionuclide to decay, i.e.

$$n_p(t = t_{1/2}) \equiv \frac{1}{2} n_{p0}. \tag{A.7}$$

From Eq. (A.6),

$$\frac{1}{2} n_{p0} = n_{p0}\exp[-\lambda_p t_{1/2}] \implies 2 = \exp[\lambda_p t_{1/2}], \tag{A.8}$$

and thus,

$$t_{1/2} = \frac{\log_e[2]}{\lambda_p}. \tag{A.9}$$

Since n_{p0} is not known a priori in most natural systems, we need to re-express Eq. (A.6) in terms of measurable quantities, i.e. n_p and the total number of daughter nuclides n_d. In the simplest case where the parent nuclide only decays to one radiogenic daughter product, we may use the relation $n_{p0} = n_p + n_d^*$ to write

$$n_p = (n_p + n_d^*)\exp[-\lambda_p t], \tag{A.10}$$

or, rearranging,

$$n_d^* \exp[-\lambda_p t] = n_p(1 - \exp[-\lambda_p t]) \implies n_d^* = n_p(\exp[\lambda_p t] - 1), \tag{A.11}$$

where n_d^* is the number of radiogenic daughter nuclides. Because most natural samples also contain some initial, non-radiogenic daughter nuclides, n_{d0}, the total number of daughter nuclides is given by $n_d = n_d^* + n_{d0}$, and we may rewrite Eq. (A.11) as

$$n_d = n_{d0} + n_p(\exp[\lambda_p t] - 1). \tag{A.12}$$

Rearranging this equation to isolate $e^{\lambda_p t}$, we get

$$\exp[\lambda_p t] = \left(\frac{n_d - n_{d0}}{n_p}\right) + 1. \tag{A.13}$$

Solving for t, we obtain the *fundamental equation of geochronology*:

$$\boxed{t = \frac{1}{\lambda_p} \log_e \left[\left(\frac{n_d - n_{d0}}{n_p} \right) + 1 \right].} \tag{A.14}$$

A.2 The K-Ar Age Equation

Of the three naturally occurring isotopes of K (^{39}K, ^{40}K , and ^{41}K), ^{40}K is the least abundant (e.g., 0.0117 $\pm$ 0.0001 atom%; Endt, 1990), and produces ^{40}Ca by beta-minus (β^-) decay and radiogenic ^{40}Ar , i.e., ^{40}Ar*, by electron capture (ε) and positron (β^+) emission[17]. To account for this 'branched' decay of ^{40}K in the case of K-Ar geochronology, we may describe the fraction of decays of parent ^{40}K that produce daughter ^{40}Ar* using the expression

$$^{40}Ar^* = \frac{\lambda_{^{40}Ar}}{\lambda} \, ^{40}K, \tag{A.15}$$

where $\lambda_{^{40}Ar}$ is the partial decay constant that accounts for the production of radiogenic ^{40}Ar by ε and β^+ decay, and λ is the total decay constant for ^{40}K . I will refer to the dimensionless quantity

$$\frac{\lambda_{^{40}Ar}}{\lambda}$$

as the branching ratio.

If we make the assumption that a system containing K formed without any inherited ^{40}Ar (i.e., $n_{d0} = 0$ in Eq. (A.14)), then the total number of daughter atoms measured equals the number produced by radioactive decay (i.e., $n_d = n_d^* \implies {}^{40}Ar = {}^{40}Ar^*$), and we may use Eq. (A.15) to rewrite Eq. (A.14) as

$$\boxed{t = \frac{1}{\lambda} \log_e \left[\frac{\lambda}{\lambda_{^{40}Ar}} \frac{^{40}Ar^*}{^{40}K} + 1 \right],} \tag{A.16}$$

which is the general age equation for the K-Ar system (Eq. (1.1)). For more details on K-Ar dating, see Dalrymple and Lanphere (1969).

A.3 The $^{40}Ar/^{39}Ar$ Age Equation

In practice, determining a date using the general K-Ar equation, Eq. (1.1), requires separate measurements of the concentrations of ^{40}Ar* and ^{40}K using two splits from a (presumably ho-

[17] Note, while Beckinsale and Gale (1969) inferred that β^+ emission contributed to the production of ^{40}Ar*, i.e., $\lambda_{^{40}Ar} = \lambda_\varepsilon + \lambda_{\beta^+}$, this decay mode is commonly considered negligible, i.e., $\lambda_{^{40}Ar} \rightarrow \lambda_\varepsilon$ (e.g., Renne et al., 2010). However, I will use $\lambda_{^{40}Ar}$ to imply that, where a non-zero value is reported, λ_{β^+} should be included in calculating $\lambda_{^{40}Ar}$.

mogeneous) sample. An alternative approach is to irradiate a single split from a sample with high-energy ('fast') neutrons, thereby converting some of the stable ^{39}K of the sample into ^{39}Ar by the ^{39}K(n,p)^{39}Ar reaction (^{39}Ar$_{\mathrm{K}}$ hereafter), and allowing a date to be determined from a single measurement. The amount of ^{39}Ar$_{\mathrm{K}}$ produced by irradiating a sample is given by

$$^{39}Ar_K = {}^{39}K\Delta T \int dE\ \phi(E)\sigma(E) \tag{A.17}$$

where ΔT is the duration of the irradiation, $\phi(E)$ is the flux of neutrons with energy E, and $\sigma(E)$ is the neutron capture cross section at energy E for the ^{39}K(n,p)^{39}Ar reaction (Mitchell, 1968; McDougall and Harrison, 1999).

For a sample with age t, Eq. (1.1) can be solved for ^{40}Ar* and written as

$$^{40}Ar^* = {}^{40}K\frac{\lambda_{^{40}Ar}}{\lambda}(\exp[\lambda t]-1). \tag{A.18}$$

Dividing both sides of Eq. (A.18) by ^{39}Ar$_{\mathrm{K}}$ and using Eq. (A.17) in the denominator of the right-hand-side, we can express the ratio of ^{40}Ar* to ^{39}Ar$_{\mathrm{K}}$ produced during neutron irradiation of the sample as

$$\left(\frac{^{40}Ar^*}{^{39}Ar_K}\right)_s = \frac{^{40}K}{^{39}K}\frac{\lambda_{^{40}Ar}}{\lambda}\frac{\exp[\lambda t]-1}{\Delta T\int dE\ \phi(E)\sigma(E)}. \tag{A.19}$$

Let us define the dimensionless factor

$$J \equiv \frac{^{39}K}{^{40}K}\frac{\lambda}{\lambda_{^{40}Ar}}\Delta T\int dE\ \phi(E)\sigma(E), \tag{A.20}$$

and rewrite Eq. (A.19) as

$$\left(\frac{^{40}Ar^*}{^{39}Ar_K}\right)_s = \frac{\exp[\lambda t]-1}{J}. \tag{A.21}$$

The factor J is commonly called the *irradiation parameter*. Solving Eq. (A.21) for t, we obtain the general ^{40}Ar/^{39}Ar age equation:

$$\boxed{t = \frac{1}{\lambda}\log_e\left[J\left(\frac{^{40}Ar^*}{^{39}Ar_K}\right)_s + 1\right].} \tag{A.22}$$

In practice, the parameters $\phi(E)$ and $\sigma(E)$ in Eq. (A.20) can be difficult to constrain. As an alternative way to determine how much ^{39}Ar$_{\mathrm{K}}$ is produced in an unknown sample, Merrihue and Turner (1966) described a method where a 'monitor' mineral with a well known age, t_m, is co-irradiated with the unknown. In this instance, we can use an equation of the form of Eq. (A.21) to

write

$$\left(\frac{^{40}Ar^*}{^{39}Ar_K}\right)_m = \frac{\exp[\lambda t_m] - 1}{J}, \tag{A.23}$$

from which it is easy to see that J can be equivalently expressed as

$$J = \frac{\exp[\lambda t_m] - 1}{(^{40}Ar^*/^{39}Ar_K)_m}. \tag{A.24}$$

Thus, the age of the unknown sample can be determined relative to the age of the monitor mineral using Eq. (A.22) and Eq. (A.24) without having to determine $\phi(E)$ and $\sigma(E)$ explicitly. For additional details on ^{40}Ar/^{39}Ar dating, see McDougall and Harrison (1999).

References

Beckinsale, R. D., Gale, N. H., 1969. A reappraisal of the decay constants and branching ratio of 40 K. Earth and Planetary Science Letters 6 (4), 289–294.

Boas, M. L., 2006. Mathematical Methods in the Physical Sciences, 3rd Edition. John Wiley & Sons, Ltd.

Dalrymple, G. B., 1979. Critical tables for conversion of K-Ar ages from old to new constants. Geology 7 (11), 558–560.

Dalrymple, G. B., Lanphere, M. A., 1969. Potassium-Argon Dating: Principles, Techniques, and Applications to Geochronology. W. H. Freeman and Company.

Endt, P. M., 1990. Energy levels of A= 21–44 nuclei (VII). Nuclear physics A 521, 1–400.

Jourdan, F., Verati, C., Féraud, G., 2006. Intercalibration of the Hb3gr ^{40}Ar/^{39}Ar dating standard. Chemical Geology 231 (3), 177–189.

Karner, D. B., Renne, P. R., 1998. ^{40}Ar/^{39}Ar Geochronology of Roman Volcanic Province Tephra in the Tiber River Valley: Age Calibration of Middle Pleistocene Sea-Level Changes. Geological Society Of America Bulletin 110 (6), 740–747.

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

Merrihue, C., Turner, G., 1966. Potassium-argon dating by activation with fast neutrons. Journal of Geophysical Research 71 (11), 2852–2857.

Mitchell, J. G., 1968. The argon-40argon-39 method for potassium-argon age determination. Geochimica et Cosmochimica Acta 32 (7), 781–790.

Nomade, S., Renne, P. R., Vogel, N., Deino, A. L., Sharp, W. D., Becker, T. A., Jaouni, A. R., Mundil, R., 2005. Alder Creek sanidine (ACs-2): A Quaternary ^{40}Ar/^{39}Ar dating standard tied to the Cobb Mountain geomagnetic event. Chemical Geology 218 (3-4), 315–338.

Renne, P. R., Mundil, R., Balco, G., Min, K., Ludwig, K. R., 2010. 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. Geochimica et Cosmochimica Acta 74 (18), 5349–5367.

Renne, P. R., Swisher, C. C., Deino, A. L., Karner, D. B., Owens, T. L., DePaolo, D. J., 1998. Intercalibration of standards, absolute ages and uncertainties in ^{40}Ar/^{39}Ar dating. Chemical Geology 145 (1), 117–152.

Rogawski, J., 2008. Multivariable Calculus. W. H. Freeman and Company.

Spell, T., McDougall, I., Aug. 2003. Characterization and calibration of ^{40}Ar/^{39}Ar dating standards. Chemical Geology 198 (3-4), 189–211.

Taylor, J. R., 1997. An Introduction to Error Analysis: The Study of Uncertainties in Physical Measurements, 2nd Edition. University Science Books.

Wendt, I., Carl, C., 1991. The statistical distribution of the mean squared weighted deviation. Chemical Geology: Isotope Geoscience section 86 (4), 275–285.

