



PROPAGATION OF ERROR FORMULAS FOR K/Ar DATING METHOD

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Received 4 June 2013

Accepted 19 March 2014

Abstract: In this paper has been derived the most relevant propagation of error formula in the case when argon peaks are measured. The most frequently cited formula published by Cox and Dalrymple deals with the isotope ratios, instead of isotope peaks heights, considered as independent variables.

Keywords: K/Ar dating, error propagation.

1. INTRODUCTION

The methods of evaluation of analytical errors in K/Ar dating method are dispersed in rather old literature (Dalrymple and Lanphere, 1969; Flisch, 1985 and Burghel, 1987). The purpose of this paper is to collect in one place the information on the evaluation of the analytical uncertainty of geological ages determined by the potassium-argon method and to correct the frequently cited error propagation formula published by Cox and Dalrymple (1967).

The propagation of error (or uncertainty) is the effect of the variables' uncertainties (or errors) on the uncertainty of a function of these variables. Under the term "uncertainty" we mean the standard deviation, σ , which is the positive square root of variance. It determines the limits around the average value of a normally distributed variable, e.g. $\langle x \rangle$, in which the true value has 68% confidence level, *i.e.* the true value can be found in the range $\langle x \rangle \pm \sigma$ with a probability of 0.68.

Let us consider the fundamental formula of K/Ar dating method (see e.g. Faure and Mensing, 2005 for its derivation):

$$t = \frac{1}{\lambda} \ln \left(1 + \frac{\lambda}{\lambda_e} \cdot \frac{{}^{40}\text{Ar}^*}{{}^{40}\text{K}} \right) \quad (1.1)$$

where λ is the total decay constant of ${}^{40}\text{K}$, λ_e is the decay constant of this isotope to ${}^{40}\text{Ar}$ by electron capture, ${}^{40}\text{Ar}^*$ is the concentration of radiogenic argon in the sample and ${}^{40}\text{K}$ is the concentration of the radioactive isotope of potassium. We will assume that the decay constants are invariant (or exact) and their values are as recommended by the IUGS Subcommittee on Geochronology (Steiger and Jäger, 1977): $\lambda = 5.543 \cdot 10^{-10} \text{ y}^{-1}$ and $\lambda_e = 0.581 \cdot 10^{-10} \text{ y}^{-1}$. The influence of small uncertainties in the decay constants were considered by Schaeffer *et al.* (1966) and Burghel (1987).

The above formula may be limited to the first order of approximation when young samples (Neogene and Paleogene) are dated:

$$t = \frac{1}{\lambda_e} \cdot \frac{{}^{40}\text{Ar}^*}{{}^{40}\text{K}} \quad (1.2)$$

Below we will consider only analytical uncertainties in ${}^{40}\text{Ar}^*$ and ${}^{40}\text{K}$ determinations, assuming that a mineral sample is not affected by inhomogeneous distribution of potassium and argon loss. These sources of errors are

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well discussed in relevant textbooks (Faure and Mensing, 2005 and Allégre, 2008).

2. UNCERTAINTY OF K/Ar DATING

Let us consider the propagation of error formula to **Eq. 1.2**. In the case of the ratio of two independent variables the simplest approach is to calculate relative standard uncertainty as a square root of sum of squared relative uncertainties (e.g. Brandt, 1999; Ku, 1969 and Propagation, 2013):

$$\frac{\sigma_t}{\langle t \rangle} = \left[\left(\frac{\sigma(^{40}\text{K})}{\langle ^{40}\text{K} \rangle} \right)^2 + \left(\frac{\sigma(^{40}\text{Ar}^*)}{\langle ^{40}\text{Ar}^* \rangle} \right)^2 \right]^{\frac{1}{2}} \quad (2.1)$$

In the case of exact **Eq. 1.1**, we can use a general form of propagation of error formula:

$$\sigma_t = \left[\left(\frac{\partial t}{\partial ^{40}\text{K}} \sigma(^{40}\text{K}) \right)^2 + \left(\frac{\partial t}{\partial ^{40}\text{Ar}^*} \sigma(^{40}\text{Ar}^*) \right)^2 \right]^{\frac{1}{2}} \\ = \frac{1}{\lambda} \cdot \frac{1}{1 + \frac{\lambda}{\lambda_e} \cdot \frac{^{40}\text{Ar}^*}{^{40}\text{K}}} \cdot \frac{\lambda}{\lambda_e} \cdot \frac{^{40}\text{Ar}^*}{^{40}\text{K}} \quad (2.2)$$

$$\left[\left(\frac{\sigma(^{40}\text{K})}{\langle ^{40}\text{K} \rangle} \right)^2 + \left(\frac{\sigma(^{40}\text{Ar}^*)}{\langle ^{40}\text{Ar}^* \rangle} \right)^2 \right]^{\frac{1}{2}}$$

Considering that $1 + \frac{\lambda}{\lambda_e} \cdot \frac{^{40}\text{Ar}^*}{^{40}\text{K}} = e^{\lambda t}$, we obtain the following expression for the relative standard uncertainty of calculated age:

$$\frac{\sigma_t}{\langle t \rangle} = \frac{1 - e^{-\lambda t}}{\lambda t} \cdot \left[\left(\frac{\sigma(^{40}\text{K})}{\langle ^{40}\text{K} \rangle} \right)^2 + \left(\frac{\sigma(^{40}\text{Ar}^*)}{\langle ^{40}\text{Ar}^* \rangle} \right)^2 \right]^{\frac{1}{2}} \quad (2.3)$$

This formula differs from the simplified formula **(2.1)** by the following time-dependent factor:

$$G = \frac{1 - e^{-\lambda t}}{\lambda t} \quad (2.4)$$

The role of this factor in the case of dating old samples was discussed by Schaeffer *et al.* (1966) and Burghelle (1987). Generally it reduces the relative uncertainty with age as is shown in **Table 1**. It should be noted that the linear approximation for the G-factor is highly convergent with the exact value up to 100 Ma.

The concentration of ^{40}K is calculated from the mass of sample, the total concentration of potassium, K, and isotope composition of natural potassium, the atomic

weight of which is 39.098304 g and the abundance of ^{40}K is 0.01167%. Thus the number ^{40}K is directly proportional to K and the relative uncertainty $\sigma(^{40}\text{K})/\langle ^{40}\text{K} \rangle$ may be replaced by $\sigma(\text{K})/\langle \text{K} \rangle$. A more serious problem is the calculation of relative uncertainty of radiogenic argon concentration $\sigma(^{40}\text{Ar}^*)/\langle ^{40}\text{Ar}^* \rangle$. The evaluation of this uncertainty is considered in the next section. Below the triangle brackets will be omitted, but their meaning “the mean value of...” in denominators of all terms of type σ_i/x will be retained.

3. EVALUATION OF $\sigma(^{40}\text{Ar}^*) / ^{40}\text{Ar}^*$

The most common method of determination of radiogenic argon is the isotopic dilution of the extracted argon with rare isotope, ^{38}Ar , called spike. We will consider that spike consists of pure ^{38}Ar , which actually contains 99.999% of this isotope (Schumacher 1975 and Schumacher 1989). Aliquots of spike are admitted to the ultra high vacuum extraction line just prior to Ar release from the dated sample. The use of a pipette system as described by Dalrymple and Lanphere (1969) directly connected to the extraction line leads to a very high precision in determination of the aliquot of ^{38}Ar spike. The amount of spike will be denoted as x , and its relative uncertainty σ_x/x may be reduced to a level of 0.3% (Cox and Dalrymple, 1967). Such high precision is achieved by calibration of x value with radiogenic argon extracted from aliquots of standards with precisely known concentration of $^{40}\text{Ar}^*$. Below we describe in detail the procedure of $^{40}\text{Ar}^*$ determination by isotopic dilution, whilst the calibration is done in reverse way. Once x_o is determined at the beginning of a series of dating, then x_t -value in subsequent dating can be expressed by the known value of “depletion constant” of the pipette, δ , and the number i :

$$x_t = x_o \delta (1 + \delta)^{-i} \quad (3.1)$$

where δ is the volume ratio of pipette to that of the spike container plus the little volume of pipette. Since $\delta \ll 1$, then expression **(3.1)** may be replaced by respective exponential form:

$$x_t = x_o \exp(-i\delta) \quad (3.2)$$

Table 1. G-factor as a function of geological age, t , parameter λ is the total decay constant of ^{40}K isotope.

t (Ma)	λt	$1 - (\lambda t)/2$ linear approxim.	$[1 - \exp(-\lambda t)]/(\lambda t)$ exact expression
100	0.055	0.973	0.973
300	0.166	0.917	0.921
500	0.277	0.862	0.873
1000	0.554	0.723	0.768
1500	0.831	0.584	0.679
3000	1.663		0.487
4000	2.217		0.402

In the determination of radiogenic argon by the spike method, we have to measure the three isotope peaks: ^{40}Ar , ^{38}Ar and ^{36}Ar . These **independent** variables will be denoted as u , v and w , respectively, whilst their relative (or percentage) uncertainties as σ_u/u , σ_v/v and σ_w/w .

Our goal now is to express the relative uncertainty $\sigma(^{40}\text{Ar}^*)/^{40}\text{Ar}^*$ which appears as a component of **Eq. 2.1** or **2.3** through the uncertainties of the four variables x , u , v , and w . Considering that $^{40}\text{Ar}^* = ^{40}\text{Ar} - (^{40}\text{Ar})_{\text{atm}} = u - Nw$ and $(^{38}\text{Ar})_{\text{spike}} = ^{38}\text{Ar} - (^{38}\text{Ar})_{\text{atm}}$, i.e. $x = v - nw$, where $N = (^{40}\text{Ar}/^{36}\text{Ar})_{\text{atm}} = 295.5$ and $n = (^{38}\text{Ar}/^{36}\text{Ar})_{\text{atm}} = 0.187$ are natural isotope ratios in atmospheric argon. From the $^{40}\text{Ar}^*$ -to- x ratio we calculate the amount of radiogenic argon:

$$^{40}\text{Ar}^* = xR \quad (3.3)$$

$$\begin{aligned} \left(\frac{\sigma_R}{R}\right)^2 &= \frac{1}{R^2} \cdot \left[\left(\frac{\partial R}{\partial u} \sigma_u\right)^2 + \left(\frac{\partial R}{\partial v} \sigma_v\right)^2 + \left(\frac{\partial R}{\partial w} \sigma_w\right)^2 \right] \\ &= \left(\frac{v - nw}{u - Nw}\right)^2 \cdot \left[\left(\frac{\sigma_u}{v - nw}\right)^2 + \left(\frac{u - Nw}{(v - nw)^2} \sigma_v\right)^2 + \left(\frac{Nv - nu}{(v - nw)^2} \sigma_w\right)^2 \right] \\ &= \frac{1}{\left(1 - N\frac{w}{u}\right)^2} \left(\frac{\sigma_u}{u}\right)^2 + \frac{1}{\left(1 - n\frac{w}{v}\right)^2} \cdot \left[\left(\frac{\sigma_v}{v}\right)^2 + \frac{\left(N\frac{w}{u} - n\frac{w}{v}\right)^2}{\left(1 - N\frac{w}{u}\right)^2} \cdot \left(\frac{\sigma_w}{w}\right)^2 \right] \end{aligned} \quad (3.6)$$

Inasmuch as $N \gg n$ whereas the ratios w/u and w/v are comparable the term Nw/u is significantly larger than nw/v and the last may be neglected. Subsequently the term $(1 - nw/v)^2$ may be replaced by its first order of approximation, $1 + 2nw/v$. Hence the above formula may be safely rewritten in the following form

$$\left(\frac{\sigma_R}{R}\right)^2 \cong \frac{1}{r^2} \cdot \left(\frac{\sigma_u}{u}\right)^2 + \left(1 + 2n\frac{w}{v}\right) \left[\left(\frac{\sigma_v}{v}\right)^2 + \left(\frac{1-r}{r}\right)^2 \cdot \left(\frac{\sigma_w}{w}\right)^2 \right] \quad (3.7)$$

where $r = 1 - Nw/u$ is the fraction of the ^{40}Ar that is radiogenic.

Combining formulas (3.5) and (3.7) we obtain

$$\left[\frac{\sigma(^{40}\text{Ar}^*)}{^{40}\text{Ar}^*}\right]^2 = \left(\frac{\sigma_x}{x}\right)^2 + \frac{1}{r^2} \cdot \left(\frac{\sigma_u}{u}\right)^2 + \left(1 + 2n\frac{w}{v}\right) \left[\left(\frac{\sigma_v}{v}\right)^2 + \left(\frac{1-r}{r}\right)^2 \cdot \left(\frac{\sigma_w}{w}\right)^2 \right] \quad (3.8)$$

A value of relative uncertainty obtained with the formula (3.8) can be substituted to equation (2.1) or (2.3) to calculate the relative uncertainty of the date calculated with formula (1.2) or (1.1), respectively.

4. DISCUSSION

We have derived a useful and simple formula for relative uncertainty of radiogenic argon determined by using aliquots of isotopically pure spike, ^{38}Ar . Note that even the spike container could be slightly contaminated by atmospheric argon, then this contamination would be corrected together with the fraction of atmospheric argon evolved in an experiment. This is a real advantage of using spike containing 99.999% of ^{38}Ar .

where the ratio R is a nonlinear function of the three remaining variables:

$$R(u, v, w) = \frac{u - Nw}{v - nw} \quad (3.4)$$

Relative standard uncertainty of $^{40}\text{Ar}^*$ can be calculated by the propagation or error formula for independent variables:

$$\left(\frac{\sigma(^{40}\text{Ar}^*)}{^{40}\text{Ar}^*}\right)^2 = \left(\frac{\sigma_x}{x}\right)^2 + \left(\frac{\sigma_R}{R}\right)^2 \quad (3.5)$$

The last term in formula (3.5) may be calculated again by the propagation or error formula applied to the linearized expression (3.4)

Cox and Dalrymple (1967) in determination of radiogenic argon by the spike method have reduced the numbers of variables to the following two isotope ratios: $^{40}\text{Ar}/^{38}\text{Ar}$ and $^{36}\text{Ar}/^{38}\text{Ar}$, which are denoted below as y and z , respectively. Although it is obviously not the case, these two variables have been treated as independent with relative uncertainties σ_y/y and σ_z/z . The appropriate formula for the ratio R of the amount of $^{40}\text{Ar}^*$ to that of $^{38}\text{Ar}_{\text{spike}}$ in terms of the newly defined variables, y and z (x remains to be the same as defined previously) is:

$$R(y, z) = \frac{y - Nz}{1 - nz} \quad (4.1)$$

where N and n have the same meaning as defined in the previous section. Relative standard uncertainty of R calculated by the propagation or error formula for independent variables is:

$$\left(\frac{\sigma_R}{R}\right)^2 = \frac{1}{R^2} \left[\left(\frac{\partial R}{\partial y}\right)^2 \sigma_y^2 + \left(\frac{\partial R}{\partial z}\right)^2 \sigma_z^2 \right] \quad (4.2)$$

Calculating the both partial derivatives and substituting them into Eq. 4.2 and the expression (4.1) for R , the following formula is obtained

$$\left(\frac{\sigma_R}{R}\right)^2 = \frac{1}{r^2} \left(\frac{\sigma_y}{y}\right)^2 + \left(\frac{1-r}{r} - \frac{1}{1-nz}\right)^2 \left(\frac{\sigma_z}{z}\right)^2 \quad (4.3)$$

$$\text{where } r = 1 - N \frac{z}{y} = 1 - N \frac{{}^{36}\text{Ar}}{{}^{40}\text{Ar}} = \frac{{}^{40}\text{Ar} - N {}^{36}\text{Ar}}{{}^{40}\text{Ar}} = \frac{{}^{40}\text{Ar}^*}{{}^{40}\text{Ar}},$$

what is the fraction of radiogenic argon. The term $(1 - nz)^{-1}$ in the first order of approximation is equal to $1 + nz$, because nz is significantly smaller than unity. Combining formulas (3.5) and (4.3) we obtain the formula derived by Cox and Dalrymple (1967):

$$\left[\frac{\sigma({}^{40}\text{Ar}^*)}{{}^{40}\text{Ar}^*}\right]^2 = \left(\frac{\sigma_x}{x}\right)^2 + \frac{1}{r^2} \left(\frac{\sigma_y}{y}\right)^2 + \left(\frac{1-r}{r} - nz\right)^2 \left(\frac{\sigma_z}{z}\right)^2 \quad (4.4)$$

It should be emphasized, that the formula derived by Cox and Dalrymple (1967) is less reliable than (3.8), because a covariance between variables y and z has been ignored. Moreover, the term $nz = 0.187({}^{36}\text{Ar}/{}^{38}\text{Ar})$ in their published formula also has been ignored.

Example. Let us consider the following output data with their standard uncertainties: $u = 2.00 \pm 0.02$, $v = 7.00 \pm 0.02$, $w = 0.002 \pm 0.00003$. For these data we have $r = 0.70$, $y = 3.50$, and $z = 0.001$. The contributions to the relative standard deviation of radiogenic argon determination $\frac{\sigma({}^{40}\text{Ar}^*)}{{}^{40}\text{Ar}^*}$, which results only from argon isotopes measurements, calculated with the two formulas (3.8) and (4.4) are 1.58% and 1.66%, respectively. Note that y and z are significantly correlated (Fig. 1), the correlation coefficient in this case is 0.53. Yet larger correlation coefficient is expected for smaller standard uncertainty of w value, which will lead to a biased value of the relative standard uncertainty calculated with Cox and Dalrymple (1967) formula.

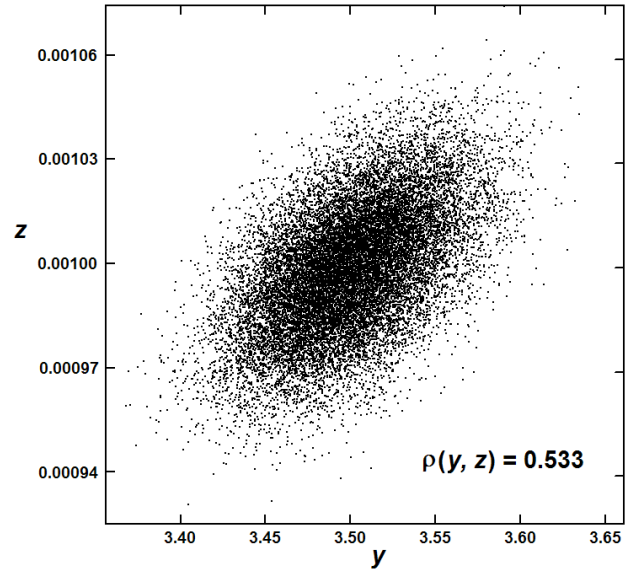


Fig. 1. The spread of y, z values calculated by the Monte Carlo method for $N = 20000$ data using average u, v, w values and their standard deviations given in the above numerical example. The correlation coefficient $\rho(y, z)$ was calculated for $N = 10^6$ y, z pairs of numbers drawn by the Monte Carlo algorithm.

5. CONCLUSION

The derived here more relevant formula (3.8) for relative error estimation of K-Ar dates should be used instead of the commonly used formula published by Cox and Dalrymple (1967) when the heights of argon peaks are determined as independent variables.

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