

## Introduction

Potassium is abundant in planetary crusts and is a major constituent of several common mineral phases, including potassium feldspar, muscovite, biotite, and hornblende. The radioactive decay of  $^{40}\text{K}$  to  $^{40}\text{Ar}$  by electron capture provides a useful chronometer and has been used to date rock samples that range in age from few thousand years to meteorites over 4.5 billion years old. Since it is difficult to accurately measure the ratio of K (a solid) to Ar (a noble gas), a portion of the radiogenic  $^{40}\text{K}$  is converted to  $^{39}\text{Ar}$  via neutron irradiation in a nuclear reactor. A fluence monitor (crystals of a known age) is packaged and irradiated alongside the unknown samples. The "known" age of the fluence monitor is used to solve for the proportion of  $^{40}\text{K}$  that has been converted to  $^{39}\text{Ar}$ , and a similar correction is applied to the unknown. The age of the unknown is then calculated using the total decay constant of  $^{40}\text{K}$  and the measured  $^{40}\text{Ar}/^{39}\text{Ar}$  ratio. This makes the  $^{40}\text{Ar}/^{39}\text{Ar}$  technique a relative dating technique, and as ages of the fluence monitors, as well as the value of the total  $^{40}\text{K}$  decay constant, are revised, legacy data that utilized previous values must be updated as well.

The two largest systematic errors in the age calculation come from the age of the fluence monitor, and the  $^{40}\text{K}$  decay constant. Fluence monitors, or standards, are chosen to match the mineral phase and age of the unknowns. Commonly used standards are the Fish Canyon Tuff sanidine, Alder Creek sanidine, GA-1550 biotite, McClure Mountain hornblende, and the "3 GR" hornblende. Fluence monitor ages may be determined from a direct  $^{40}\text{K}$ - $^{40}\text{Ar}$  measurement (e.g. McDougall and Roksandic, 1974), by intercalibration with another method such as astronomical tuning (Renne et al., 1998; Kuiper et al., 2008) or U-Pb (Mundil et al. 2006), or by inter-calibration with other  $^{40}\text{Ar}/^{39}\text{Ar}$  standards (e.g. Renne et al., 1998). Values in the literature for these ages have changed through time as more precise determinations and more statistical calculations have been performed.

For instance, Fish Canyon sanidine (or FCs) was first proposed as a standard by Cebula (1986) with an age of 27.79 Ma relative to a McClure Mountain hornblende (MMhb-1) age of 518.9 Ma. When the MMhb-1 date was revised to 520.4 Ma, the FCs age increased to 27.84 Ma, which was used until Renne et al. (1994) published an age of 28.02 Ma determined by inter-calibration of FCs with the astronomical time scale—measured by counting periodic variations in sediments produced by Milankovic cycles. A new FCs date was recently published by Kuiper et al. (2008) based on inter-calibration with the astronomical time scale in a different sedimentary basin and a more recent decay constant determination, yielding what is thought to be a more precise age of 28.201 Ma  $\pm$  0.046 Ma.

The total  $^{40}\text{K}$  decay constant is the sum of the electron capture decay constant, which produces  $^{40}\text{Ar}$ , and the beta decay constant, which produces  $^{40}\text{Ca}$ .  $^{40}\text{Ca}$  is so abundant in nature that the radiogenic  $^{40}\text{Ca}$  signal is overwhelmed, but  $^{40}\text{Ar}$  is only produced by radioactive decay of  $^{40}\text{K}$ . Although the electron capture and

beta particle decay constants must be considered separately for first principles dating of standards, their ratio can be eliminated when comparing the unknown to a standard during data reduction, leaving only the total decay constant in the expression for the age of the unknown (see below). The total decay constant has been refined numerous times. Beckinsale and Gale (1969) compiled several measurements of the branching ratio and decay constants, choosing the most reliable methods and weighting the chosen measurements by the inverse of their variance, yielding  $5.480 \times 10^{-10} \text{ yr}^{-1}$ . Steiger and Jager (1977) with the Subcommittee on Geochronology at the 1976 IGC meeting, revised the Beckinsale and Gale decay constant with newer K isotope abundances measured by Garner et al. (1976) to determine a value of  $5.543 \times 10^{-10} \text{ yr}^{-1}$ . Endt and Van der Leun (1973) also compiled activity data and included several more recent measurements, publishing a value of  $5.428 \times 10^{-10} \text{ yr}^{-1}$ . The Steiger and Jaeger value is commonly accepted.

Min et al. (2000) revisited both compilations. Based on their comparisons with Ar data from the Vesuvius eruption and the U-Pb data from the Palisade Rhyolite, Min et al. choose an updated value and uncertainty of the Endt and Van der Leun decay constant as being "most realistic",  $5.463 \pm 0.214 \times 10^{-10} \text{ yr}^{-1}$ . Kuiper et al (2009) used the latter decay constant when re-calibrating the FCs to the astronomical time scale, and Ar/Ar geochronologists at the 2009 EARTHTIME IV voted to adopt this value in future publications.

## Calculations

In order to compare between  $^{40}\text{Ar}/^{39}\text{Ar}$  ages, each age determination must use the same decay constant and the same fluence monitor age, or fluence monitor ages that have been inter-calibrated (Baksi et al., 1996; Renne et al., 1998). To convert legacy data into the same reference frame, the previous decay constant and standard age are needed, as well as the new values. Min et al. (2000) decay constant uncertainties are less precise (although hopefully more accurate) than those of Steiger and Jager, but newer FCs age determinations are more precise. Propagating the systematic uncertainty resulting from the standard age uncertainty and the decay constant uncertainty can take these into account to yield an absolute age uncertainty. In this case, the J value of the fluence monitor (a measure of the neutron flux of the standard) is required for accurate error propagation.

The expression for the age of an unknown re-calculated with a new decay constant and fluence monitor age can be derived from the following variables:

<b>Legacy Data:</b>	
$\left(\frac{^{40}\text{Ar}}{^{39}\text{Ar}}\right)_{std}, \left(\frac{^{40}\text{Ar}}{^{39}\text{Ar}}\right)_{spl}$	Measured ratio of radiogenic $^{40}\text{Ar}$ to $^{39}\text{Ar}$ in the standard and unknown sample, corrected for fractionation, blank, and interferences
$\lambda_{old}$	Decay constant used in legacy calculation
$J_{old}$	J value for legacy data (used only in derivation)
$t_{std, old}, t_{spl, old}$	Age of the standard and sample, reported in legacy data
<b>Converted Data:</b>	
$\lambda_{new}$	New decay constant for calculation
$J_{new}$	New J value (used only in derivation)
$t_{std, new}, t_{spl, new}$	New age of standard (input) and sample (calculated)

Formulas for the  $^{40}\text{Ar}/^{39}\text{Ar}$  ratio for the standard and the sample, as determined in the legacy data, come directly from the  $^{40}\text{Ar}/^{39}\text{Ar}$  age equation (1):

$$J \cdot \left( \frac{^{40}\text{Ar}}{^{39}\text{Ar}} \right) = e^{\lambda \cdot t} - 1 \quad (1)$$

$$\left( \frac{^{40}\text{Ar}}{^{39}\text{Ar}} \right)_{std} = \frac{e^{\lambda_{old} \cdot t_{std, old}} - 1}{J_{old}} \quad (2)$$

$$\left( \frac{^{40}\text{Ar}}{^{39}\text{Ar}} \right)_{spl} = \frac{e^{\lambda_{old} \cdot t_{spl, old}} - 1}{J_{old}} \quad (3)$$

Again using equation (1), an expression for the newly recalculated J value,  $J_{new}$ , includes the new decay constant, new standard date, and new unknown age, as well as the  $^{40}\text{Ar}/^{39}\text{Ar}$  ratio of the standard. The expression for  $^{40}\text{Ar}/^{39}\text{Ar}_{std}$  from equation (2) can then be substituted into the denominator.

$$J_{new} = \frac{e^{\lambda_{new} \cdot t_{std, new}} - 1}{\left( \frac{^{40}\text{Ar}}{^{39}\text{Ar}} \right)_{std}} = \frac{J_{old} \cdot (e^{\lambda_{new} \cdot t_{std, new}} - 1)}{(e^{\lambda_{old} \cdot t_{std, old}} - 1)} \quad (4)$$

Equation 1 can now be solved for  $t$ , the age of the unknown sample, in terms of the known legacy data variables and the new fluence monitor age and decay constant. Equation (1) becomes:

$$t_{spl, new} = \frac{1}{\lambda_{new}} \ln \left[ J_{new} \cdot \left( \frac{^{40}\text{Ar}}{^{39}\text{Ar}} \right)_{spl} + 1 \right] \quad (5)$$

where  $\ln$  is the natural logarithm. Substituting the expression for  $J_{new}$  in equation (4) and the expression for  $^{40}\text{Ar}/^{39}\text{Ar}_{std}$  from equation (2):

$$t_{spl, new} = \frac{1}{\lambda_{new}} \ln \left[ \frac{J_{old} \cdot (e^{\lambda_{new} \cdot t_{std, new}} - 1)}{(e^{\lambda_{old} \cdot t_{std, old}} - 1)} \cdot \frac{(e^{\lambda_{old} \cdot t_{spl, old}} - 1)}{J_{old}} + 1 \right] \quad (6)$$

The  $J_{old}$  values in the numerator and denominator of (6) cancel, yielding:

$$t_{spl, new} = \frac{1}{\lambda_{new}} \ln \left[ \frac{(e^{\lambda_{new} \cdot t_{std, new}} - 1)(e^{\lambda_{old} \cdot t_{spl, old}} - 1)}{(e^{\lambda_{old} \cdot t_{std, old}} - 1)} + 1 \right]$$

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