

NEW MEXICO GEOCHRONOLOGY RESEARCH LABORATORY

K/AR AND $^{40}\text{Ar}/^{39}\text{Ar}$ METHODS

Isotopes of Potassium and Argon

The isotopes the KAr system relies on are Potassium (K) and Argon (Ar). Potassium, an alkali metal, the Earth's eighth most abundant element is common in many rocks and rock-forming minerals. The quantity of potassium in a rock or mineral is variable proportional to the amount of silica present. Therefore, mafic rocks and minerals often contain less potassium than an equal amount of silicic rock or mineral. Potassium can be mobilized into or out of a rock or mineral through alteration processes. Due to the relatively heavy atomic weight of potassium, insignificant fractionation of the different potassium isotopes occurs. However, the ^{40}K isotope is radioactive and therefore will be reduced in quantity over time. But, for the purposes of the KAr dating system, the relative abundance of ^{40}K is so small and its half-life is so long that its ratios with the other Potassium isotopes are considered constant.

Natural abundance of potassium and argon

$$^{39}\text{K} = 93.2581 \pm 0.0029\%$$

$$^{40}\text{K} = 0.01167 \pm 0.00004\%$$

$$^{41}\text{K} = 6.7302 \pm 0.0029\%$$

$$^{40}\text{Ar} = 99.60\%$$

$$^{38}\text{Ar} = 0.063\%$$

$$^{36}\text{Ar} = 0.337\% \quad (^{40}\text{Ar}/^{36}\text{Ar} = 295.5)$$

Argon, a noble gas, constitutes approximately 0.1-5% of the Earth's present day atmosphere. Because it is present within the atmosphere, every rock and mineral will have some quantity of Argon. Argon can mobilized into or out of a rock or mineral through alteration *and* thermal processes. Like Potassium, Argon cannot be significantly fractionated in nature. However, ^{40}Ar is the decay product of ^{40}K and therefore will increase in quantity over time. The quantity of ^{40}Ar produced in a rock or mineral over time can be determined by subtracting the amount known to be contained in the atmosphere. This is done using the constant $^{40}\text{Ar}/^{36}\text{Ar}$ ratio of atmospheric Argon. This ratio is 295.5.

Radioactive decay of parent isotope to daughter isotope

The nuclei of naturally occurring ^{40}K is unstable, decaying at a constant rate (half-life = 1.25 billion years). The decay scheme is electron capture and positron decay. About 89% of the ^{40}K atoms will decay to ^{40}Ca . For the K/Ar dating system, this decay scheme to calcium isotopes is ignored. The remaining 11% of the ^{40}K atoms decay to ^{40}Ar . It is this scheme that makes the K/Ar method work.

The buildup of radiogenic ^{40}Ar ($^{40}\text{Ar}^*$) in a closed system can be expressed by the equation:

$$^{40}\text{Ar}^* = \frac{\lambda_e}{\lambda} {}^{40}\text{K}(e^{\lambda t} - 1)$$

where: $^{40}\text{Ar}^*$ = the number of 40 Argon atoms after time t
 ^{40}K = the number of 40 Potassium atoms
 λ_e = decay constant of ^{40}K to ^{40}Ar
 λ = total decay constant of ^{40}K
t = time
e = logarithm to the base e

The K/Ar Dating technique

General assumptions for the Potassium-Argon dating system

Certain assumptions must be satisfied before the age of a rock or mineral can be calculated with the Potassium-Argon dating technique. These are:

- The material in question is a closed system. In other words, no radiogenic ^{40}Ar has escaped from the rock/mineral since it formed. In the case of a volcanic mineral, this means rapid cooling. Likewise, potassium has not been gained or lost.
- A correction is made for atmospheric argon (^{40}Ar from the $^{40}\text{Ar}/^{36}\text{Ar}$ ratio = 295.5 subtracted).
- No non-atmospheric ^{40}Ar was incorporated into the rock/mineral during or after its formation.

- The isotopes of potassium in the rock/mineral have not fractionated, except by ^{40}K decay.
- The decay constants of ^{40}K are accurately known.
- The quantities of ^{40}Ar and potassium in the rock/mineral are accurately determined.

The K/Ar age determination

Once the ^{40}Ar and potassium in a rock/mineral are accurately measured, the amount of ^{40}K (based on the relative abundance of ^{40}K to total potassium) and $^{40}\text{Ar}^*$ (radiogenic ^{40}Ar) must be calculated. The K/Ar method uses a spike (known quantity) of ^{38}Ar mixed with the argon extracted from the rock/mineral to determine the quantity of $^{40}\text{Ar}^*$. The resulting $^{40}\text{Ar}^*$ and ^{40}K can be plugged into the age equation as follows:

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

where: t = age
 λ = total decay constant of ^{40}K
 λ_e = decay constant of ^{40}K to ^{40}Ar
 $^{40}\text{Ar}^*$ = ^{40}Ar produced by *in situ* decay of ^{40}K (Daughter)
 ^{40}K = $^{40}\text{Potassium}$ (Parent)

Problems and Limitations of the K/Ar dating technique

Because the K/Ar dating technique relies on the determining the absolute abundances of both ^{40}Ar and potassium, there is not a reliable way to determine if the assumptions are valid. Argon loss and excess argon are two common problems that may cause erroneous ages to be determined. Argon loss occurs when radiogenic ^{40}Ar ($^{40}\text{Ar}^*$) produced within a rock/mineral escapes sometime after its formation. Alteration and high temperature can damage a rock/mineral lattice sufficiently to allow $^{40}\text{Ar}^*$ to be released. This can cause the calculated K/Ar age to be younger than the "true" age of the dated material. Conversely, excess argon ($^{40}\text{Ar}_E$) can cause the calculated K/Ar age to be older than the "true" age of the dated material. Excess argon is simply ^{40}Ar that is attributed to radiogenic ^{40}Ar and/or atmospheric ^{40}Ar . Excess argon may be derived from the mantle, as bubbles trapped in

a melt, in the case of a magma. Or it could be a xenocryst/xenolith trapped in a magma/lava during emplacement.

The $^{40}\text{Ar}/^{39}\text{Ar}$ Dating technique

Principles of the $^{40}\text{Ar}/^{39}\text{Ar}$ method

The $^{40}\text{Ar}/^{39}\text{Ar}$ dating technique is a more sophisticated variation of the K/Ar dating technique. Both techniques rely on the measurement of a daughter isotope (^{40}Ar) and a parent isotope. While the K/Ar technique measures potassium as the parent, the $^{40}\text{Ar}/^{39}\text{Ar}$ technique uses ^{39}Ar .

Because the relative abundances of the potassium isotopes are known, the $^{39}\text{Ar}_k$ (produced from ^{39}K by a fast neutron reaction) can be used as a proxy for potassium. Therefore, unlike the conventional K/Ar technique, absolute abundances need not be measured. Instead, the ratios of the different argon isotopes are measured, yielding more precise and accurate results. Additional advantages of the single isotopic measurements of the $^{40}\text{Ar}/^{39}\text{Ar}$ technique are decreased effects of sample inhomogeneity and the use of smaller sample sizes.

Sample Irradiation / Production of ^{39}Ar

Because $^{39}\text{Ar}_k$ can only be produced by a fast neutron reaction on ^{39}K [$^{39}\text{K}(n,p)^{39}\text{Ar}$], all samples dated by the $^{40}\text{Ar}/^{39}\text{Ar}$ technique must be irradiated in the core of a nuclear reactor. The amount of $^{39}\text{Ar}_k$ produced in any given irradiation will be dependant on the amount of ^{39}K present initially, the length of the irradiation, the neutron flux density and the neutron capture cross section for ^{39}K . However, because each of these parameters is difficult to determine independantly, a mineral standard, or monitor, of known age is irradiated with the samples of unknown age. The monitor flux can then be extrapolated to the samples, thereby determining their flux. This flux is known as the 'J' and can be determined by the following equation:

$$J = \frac{e^{\lambda t_m} - 1}{^{40}\text{Ar}^*/^{39}\text{Ar}}$$

where: J = irradiation flux parameter
 $^{40}\text{Ar}^*/^{39}\text{Ar}$ = the measured ratio in monitor
 t_m = age of flux monitor
 λ = total decay constant of ^{40}K
e = logarithm to the base e

In addition to ^{39}Ar production from ^{39}K , several other 'interference' reactions occur during irradiation of the samples. Other isotopes of argon are produced from potassium, calcium, argon and chlorine. These are:

Argon Produced	Calcium	Potassium	Argon	Chlorine
^{36}Ar	^{40}Ca	—	—	—
^{37}Ar	^{40}Ca	^{39}K	^{36}Ar	—
^{38}Ar	^{42}Ca	^{39}K ^{41}K	^{40}Ar	^{37}Cl
^{39}Ar	^{42}Ca ^{43}Ca	^{39}K ^{40}K	^{38}Ar ^{40}Ar	—
^{40}Ar	^{43}Ca ^{44}Ca	^{40}K ^{41}K	—	—

Beneficial reactions Undesirable reactions
 Insignificant reactions

As the table above illustrates, several "undesirable" reactions occur on isotopes present within every geologic sample. These reactor produced isotopes of argon must be corrected for in order to determine an accurate age. The monitoring of the interfering reactions is performed through the use of laboratory salts and glasses. For example, to determine the amount of reactor produced ^{40}Ar from ^{40}K , potassium-rich glass is irradiated with the samples. The $^{40}\text{Ar}/^{39}\text{Ar}$ ratio of the glass is then measured in the mass spectrometer to determine the correction factor that must be applied to the rest of the samples in that irradiation. CaF is also routinely irradiated and measured to determine the $^{36}\text{Ar}/^{37}\text{Ar}$ and $^{39}\text{Ar}/^{37}\text{Ar}$ correction factors. The "desirable" production of ^{37}Ar from ^{40}Ca allows us determine how much ^{36}Ar and ^{39}Ar to correct for, as well as the K/Ca ratio of the sample. The desirable production of ^{38}Ar from ^{37}Cl allows us to

determine how much chlorine is present in our samples. A salt of KCl is irradiated to determine the $^{38}\text{Ar}/^{39}\text{Ar}$ production ratio which can then be applied to other samples to determine K/Cl ratios.

$^{40}\text{Ar}/^{39}\text{Ar}$ age determination

Once the J (neutron flux parameter), $^{40}\text{Ar}^*$ and $^{39}\text{Ar}_k$ have been determined (ie. subtracting atmospheric argon, system blank and interfering reactor produced isotopes), they can be included in the $^{40}\text{Ar}/^{39}\text{Ar}$ age equation:

$$t = \frac{1}{\lambda} \ln \left(\frac{^{40}\text{Ar}^*}{^{39}\text{Ar}} J + 1 \right)$$

where: t = age

λ = total decay constant of ^{40}K

J = neutron flux constant

$^{40}\text{Ar}^*$ = $^{40}\text{Argon}$ produced by *in situ* decay of ^{40}K (Daughter)

^{39}Ar = $^{39}\text{Argon}$ produced by neutron activation of ^{39}K (Parent)

Because the $^{40}\text{Ar}/^{39}\text{Ar}$ technique relies on ratios instead of absolute quantities, we are able to extract and measure multiple aliquots of argon from a single sample. Multiple argon extractions can be performed on a sample in several ways. Step-heating is the most common way and involves either a furnace or a laser to uniformly heat the sample to evolve argon. The individual ages from each heating step are then graphically plotted on an age spectrum or an isochron. Mechanical crushing is also a technique capable of releasing argon from a single sample in multiple steps.

Laser probes also allow multiple ages to be determined on a single sample aliquot, but do so using accurate and precise spatial control. For example, laser spot sizes of 100 microns or less allow a user to extract multiple argon samples from across a small mica or feldspar grain. The results from a laser probe can be plotted in several graphical ways, including a map of a grain showing lateral argon distribution.

$^{40}\text{Ar}/^{39}\text{Ar}$ total fusion of a sample is comparable to a K/Ar age determination in that it relies on wholesale release of argon at one time. However, unlike conventional K/Ar, $^{40}\text{Ar}/^{39}\text{Ar}$ total fusion measures ratios, making it ideal for samples known to be

very argon retentive (eg. sanidine). Total fusion is performed using a laser and results are commonly plotted on probability distribution diagrams or ideograms.

Some problems with the $^{40}\text{Ar}/^{39}\text{Ar}$ technique.

Standard Intercalibration

In order for an age to be calculated by the $^{40}\text{Ar}/^{39}\text{Ar}$ technique, the J parameter must be known. For the J to be determined, a standard of known age must be irradiated with the samples of unknown age. Because this (primary) standard ultimately cannot be determined by $^{40}\text{Ar}/^{39}\text{Ar}$, it must be first determined by another isotopic dating method. The method most commonly used to date the primary standard is the conventional K/Ar technique. The primary standard must be a mineral that is homogeneous, abundant and easily dated by the K/Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ methods. Traditionally, this primary standard has been a hornblende from the McClure Mountains, Colorado (a.k.a. MMhb-1). Once an accurate and precise age is determined for the primary standard, other minerals can be dated relative to it by the $^{40}\text{Ar}/^{39}\text{Ar}$ method. These secondary minerals are often more convenient to date by the $^{40}\text{Ar}/^{39}\text{Ar}$ technique (e.g. sanidine). However, while it is often easy to determine the age of the primary standard by the K/Ar method, it is difficult for different dating laboratories to agree on the final age. Likewise, because of heterogeneity problems with the MMhb-1 sample, the K/Ar ages are not always reproducible. This imprecision (and inaccuracy) is transferred to the secondary minerals used daily by the $^{40}\text{Ar}/^{39}\text{Ar}$ technique. Fortunately, other techniques are available to re-evaluate and test the absolute ages of the standards used by the $^{40}\text{Ar}/^{39}\text{Ar}$ technique. Some of these include other isotopic dating techniques (e.g. U/Pb) and the astronomical polarity time scale (APTS).

Decay Constants

Another issue affecting the ultimate precision and accuracy of the $^{40}\text{Ar}/^{39}\text{Ar}$ technique is the uncertainty in the decay constants for ^{40}K . This uncertainty results from 1) the branched decay scheme of ^{40}K and 2) the long half-life of ^{40}K (1.25 billion years). As technology advances, it is likely that the decay constants used in the $^{40}\text{Ar}/^{39}\text{Ar}$ age equation will become continually more refined allowing much more accurate and precise ages to be determined.

J Factor

Because the J value is extrapolated from a standard to an unknown, the accuracy and precision on that J value is critical. J value uncertainty can be minimized by constraining the geometry of the standard relative to the unknown, both vertically and horizontally. The NMGRl does this by irradiating samples in machined aluminum disks where standards and unknowns alternate every other position. J error can also be reduced by analyzing more flux monitor aliquots per standard location.

³⁹Ar Recoil

The effects of irradiation on potassium-bearing rocks/minerals can sometimes result in anomalously old apparent ages. This is caused by the net loss of ³⁹Ar_k from the sample by recoil (the kinetic energy imparted on a ³⁹Ar_k atom by the emission of a proton during the (n,p) reaction). Recoil is likely in every potassium-bearing sample, but only becomes a significant problem with very fine grained minerals (e.g. clays) and glass. For multi-phase samples such as basaltic whole rocks, ³⁹Ar_k redistribution may be more of a problem than net ³⁹Ar_k loss. In this case, ³⁹Ar may recoil out of a low-temperature, high-potassium mineral (e.g. K-feldspar) into a high-temperature, low potassium mineral (e.g. pyroxene). Such a phenomenon would greatly affect the shape of the age spectrum.

References

1. McDougall, I., and Harrison, T.M., 1999, Geochronology and thermochronology by the ⁴⁰Ar/³⁹Ar method: New York, Oxford University Press, xii, 269 p.

<https://geoinfo.nmt.edu/labs/argon/methods/home.html>