The K-Ar-Ca system

We have now discussed many of the basic aspects of radiogenic isotope geochemistry and we can now consider how it is applied to solving questions about the Earth. We will begin by discussing geochronology, because this aspect is basic to other aspects of isotope geochemistry. To understand the more chemical and geological aspects of isotope geochemistry, we must first learn to tell time, so to speak. We will consider the various decay systems separately. Except for some special aspects of K-Ar and U-Th-Pb, the principles involved do not differ between these systems. The differences that do exist arise from the different chemical behavior of the elements involved.

Two aspects of K-Ar-Ca system make it special. First, it is a branched decay: a \(^{40}\)K nucleus (an odd-odd nuclide) may decay to either a \(^{40}\)Ca by \(\beta^-\) or to a \(^{40}\)Ar atom by electron capture (or much more rarely by positron emission — which is just as well for us). It is impossible to predict how a given \(^{40}\)K atom will decay, just as it is impossible to predict when it will decay. We can predict quite accurately what proportion of a large number of \(^{40}\)K atoms will decay to each, however. The ratio of electron captures to beta decays is called the branching ratio and is defined as:

\[
R = \frac{\lambda_e}{\lambda_\beta} \quad 4.1
\]

where the two lambda's are the decay constants (i.e., the probability of decay) for each mode. The branching ratio is 0.117, \(\lambda_e = 0.581 \times 10^{-10}\) yr, \(\lambda_\beta = 4.962 \times 10^{-10}\) yr. The total decay constant for \(^{40}\)K is:

\[
\lambda = \lambda_\beta + \lambda_e = 5.543 \times 10^{-10}\text{yr}^{-1} \quad 4.2
\]

We need to take account of this branched decay in our equation, because while K decaying to Ca does not produce radiogenic Ar, it is no longer K and not available for \(^{40}\)Ar production. Thus our equation for radiogenic daughter production (equation 3.7) becomes:

\[
^{40}\text{Ar}^* = \frac{\lambda_e}{\lambda} \times ^{40}\text{K} (e^{\lambda t} - 1) \quad 4.3
\]

where the asterisk indicates radiogenic \(^{40}\)Ar. Note we can write a similar equation for \(^{40}\)Ca by substituting \(\lambda_\beta\) for \(\lambda_e\).

Most, although not all, of the work on the K-Ca-Ar system has focused on Ar because the \(^{40}\)K/\(^{40}\)Ca ratio is usually small. \(^{40}\)K is the least abundant of the K isotopes (0.012%), whereas \(^{40}\)Ca is the most abundant \(^{40}\)Ca isotope (96.92%), and Ca is a more abundant element than K (\(^{40}\)Ca is even-even, \(^{40}\)K is odd-odd). As a result, variations in the \(^{40}\)Ca/\(^{42}\)Ca ratio resulting from radioactive decay are quite small and difficult to measure. Only in very favorable circumstances, such as halide salt deposits, is geochronology practical.

As one might expect, particularly in view of the above discussion, one of the most important criteria for a useful radiometric chronometer is that the variations in the radiogenic isotope be large relative to the precision and accuracy with which they can be measured. In this respect, a short half-life is advantageous, and K has one of the shortest half-lives of the long-lived radioactive isotopes. Because of the volatility of Ar, the Earth either lost much of its Ar during its formation, or never acquired much, giving the Earth a rather high K/Ar ratio. Furthermore, much of the Ar the Earth retained is now in the atmosphere. As a result, \(^{40}\)K/\(^{40}\)Ar ratios in the solid Earth tend to be quite high. Because of the high \(^{40}\)K/\(^{40}\)Ar ratios and the relatively short half-life of \(^{40}\)K, the K-Ar system is often the one of choice when the task at hand is to date very young events. Meaningful ages (‘meaningful’ means the uncertainty is small relative to the age) of less than 30,000 years have been determined in favorable circumstances. \(^{40}\)K/\(^{40}\)Ar it is the only long-lived decay system that has produced age information of use in archeology and human evolution.

Much of what is special about K-Ar derives from Ar being a noble gas and its resulting refusal to be chemically bound in crystal lattices. Ar in rocks and minerals is simply trapped there. It has difficulty
escaping because the atoms of the lattice block its escape path, but it is does not form chemical bonds with other atoms in the lattice. Thus when a mineral crystallizes from a lava, it will generally, although not always, do so with very little Ar. Pillow basalts formed on the seafloor are one example of exceptions to this rule. The combination of relatively high pressure and rapid transition from the liquid to the solid state can result in trapping of substantial amounts of Ar. Similarly, minerals crystallizing from plutonic rocks may also retain Ar.

In favorable circumstances, essentially no Ar will be trapped in a mineral crystallizing from lava. The great advantage of this, from a geochronological viewpoint, is we have only one unknown, namely \( t \), and we can use equation 4.3 to solve for it by measuring the \(^{40}\text{K}\) and \(^{40}\text{Ar}\) in one sample. Actually, one need not assume that no ‘initial’ Ar whatsoever is present. Indeed, in detail, this would seem a poor assumption since a mineral crystallizing in contact with the atmosphere can be expected to absorb a small but finite amount of atmospheric Ar. For relatively young samples, this atmospheric Ar is readily corrected for since the atmosphere has a uniform ratio \(^{40}\text{Ar}/^{36}\text{Ar}\) of 295.5. By measuring the amount of \(^{36}\text{Ar}\) present, we can deduce the amount of atmospheric \(^{40}\text{Ar}\) initially present. Our age equation (equation 4.17) becomes simply:

\[
\frac{^{40}\text{Ar}}{^{36}\text{Ar}} = 295.5 + \frac{\lambda_c}{\lambda} \frac{^{40}\text{K}}{^{36}\text{Ar}} (e^{t Lamda} - 1)
\]

If we suspect that the composition of ‘initial’ Ar differs significantly from atmospheric, it is then necessary to employ the isochron approach, measuring K and Ar in a number of cogenetic samples and solving simultaneously for \( t \) and the initial \(^{40}\text{Ar}/^{36}\text{Ar}\) ratio.

**Diffusion, Cooling Rates, and Closure Temperatures**

Because Ar is not chemically bound in lattices, the K-Ar clock will generally be reset more readily than other systems. We concluded earlier that an event that ‘resets’ a radiometric clock is generally a thermal one. In the case of K-Ar, we might guess that the system would be reset whenever temperatures are high enough to allow Ar to diffuse out of the rock or mineral of interest. It is worth considering this on a slightly more quantitative level.

It can be shown both theoretically and experimentally that the rate at which a species will diffuse through a medium is related exponentially to temperature:

\[
D = D_0 e^{-E_A/R_T}
\]

where \( D \) is the diffusion coefficient, \( D_0 \) is the ‘frequency factor’, \( E_A \) is the activation energy, \( R \) is the gas constant and \( T \) is thermodynamic, or absolute, temperature, (i.e., kelvins). The diffusion ‘flux’ is related to the concentration gradient by Fick’s First Law:

\[
J = -D \left( \frac{\partial C}{\partial x} \right)
\]

where \( C \) is the concentration and \( x \) is distance. Figure 4.1 shows a plot of experimentally determined values of \( D \) for Ar in biotite plotted against the inverse of temperature. The point to be made here is that relatively small increases in temperature result in large increases in the diffusion coefficient. For example, increasing the temperature from 600° C to 700° C results in a two order of magnitude increase of the diffusion coefficient, and, for a given concentration gradient, of the Ar diffusion flux. Using the values of \( E_A \) and \( D_0 \) given in the figure, we can calculate the diffusion coefficient for temperatures not shown in the graph. The value of \( R \) is 1.987 cal/Kelvin-mole (8.314 joules/Kelvin-mole). For a temperature of 300 K (27°C), \( D \) would be \( 4 \times 10^{-36} \) cm^2/sec. For any reasonable concentration gradient, there would be no significant Ar loss from biotite, even over extremely long times. At 600 K (327°C), we obtain \( D = 6 \times 10^{-19} \) cm^2/sec, which implies a slow, but significant diffusion rate. At 700° C, however, loss of Ar would be quite rapid: about 1/3 of the Ar would be lost from biotites of 97µ radius in 2-
The following equation (from Crank, 1975) is of use in interpreting diffusion coefficients. The equation gives the fraction of the species lost as a function of time ($t$), diffusion coefficient, and the diffusion radius ($a$).

$$f \equiv \frac{4}{\pi^{1/2}} \left( \frac{Dt}{a^2} \right)^{1/2} - \frac{Dt}{a^2} - \frac{1}{3\pi^{1/2}} \left( \frac{Dt}{a^2} \right)^{3/2}$$

The equation assumes radial diffusion in a cylinder of infinite length and radius $a$. We can use this equation to understand how Ar loss will vary with temperature. We assume a value for $a$ of 150 μ, and use the $D_o$ and $E_A$ values given in Figure 4.1. Figure 4.2 shows the results of this calculation performed for various times (and at various temperatures: $D$ is a function of temperature, of course).

Let’s consider the geological implications of this diagram. Imagine a body of rock, either igneous or metamorphic, cooling from high temperature, a temperature high enough so that all Ar is lost. Let’s pick up the story when the body is still 400°C and cooling at a rate of 100°C/Ma. At this temperature, the biotite would just be beginning to retain radiogenic Ar; that is, it is not being lost quite as fast as it is being created. After the first additional million years, it would have cooled to 300°C, and biotite would be retaining most of its radiogenic Ar (loss rate of about 10 percent per Ma). If cooling continues at this rate for another million years (in the real world, it is unlikely cooling rates would be so constant), biotite would be loosing Ar at a rate of only a tenth of a percent per Ma, a fairly insignificant rate. If the body then cooled completely, and if we sampled biotite for K-Ar dating some 100 Ma later, assuming the biotite was not reheated, the ‘age’ we would calculate would refer to that 2 Ma period when the biotite cooled from 400°C to 200°C, and probably closer to the time it passed from 400°C to 300°C. We say the biotite ‘closed’ at that time, and we can estimate the closure temperature at between 300°C and 400°C.

Suppose cooling was slower, say 10°/Ma. In this case, 10 Ma would be required to cool from 400°C to 300°C, and 20 Ma to cool to 200°C. A much smaller fraction of the radiogenic Ar produced while the biotite was in the 200-400°C range would have been retained. The ‘age’ we would calculate using equation 4.4 would be younger than in the example above. It would thus seem that under these circumstances, the ‘closure temperature’ would depend on the cooling rate. This is indeed the case.

Dodson (1973) derived an equation for ‘closure temperature’ (also sometimes called blocking temperature) as a function of diffusion parameters, grain size and shape, and cooling rate:

$$T_c = \frac{E_A}{R \ln \left( \frac{ART^2D_o}{a^2E_A\tau} \right)}$$

3 weeks (you can understand then why the experiments were done at these temperatures and not lower ones).

*Note that this equation implies that diffusional loss will be inversely related to crystal size: larger crystals will lose less.
where $\tau$ is the cooling rate, $a$ is the characteristic diffusion dimension (e.g., radius of a spherical grain), and $A$ is a geometric factor (equal to 55 for a sphere, 27 for a cylinder, and 9 for a sheet). Unfortunately, this is not directly solvable since $T_c$ occurs both in and out of the log, but it can be solved by indirect methods.$^\dagger$

There are several important notions we can come away with. First, a ‘closure temperature’ is a useful concept, but a mineral will not suddenly stop losing Ar, or any other radiogenic component, at its closure temperature. Closure temperature reflects a trade off between loss and creation of the radiogenic component. Second, there is some ultimate geological limitations on the meaning of an age of a slowly cooled rock, such as a large intrusion or regionally metamorphosed body of rock. We might also expect the age we obtain will depend on the mineral we use for dating (since the diffusion coefficient will vary), and perhaps on its composition (there is in fact some compositional dependence of the Ar diffusion coefficient on the Fe/Mg ratio in biotite; but apparently none in hornblende). Finally, we get the sense that it might be rather easy for K-Ar mineral age to be partially reset. This is certainly the case. We discuss next a technique that can at least identify partially reset minerals, and in favorable cases, provide a reasonable estimate of the original ‘age’.

$^{40}$Ar-$^{39}$Ar Dating

If you look at the table of isotopes you’ll see $^{39}$Ar has a half-life of 269 years and does not occur naturally. You might justifiably wonder how it could be used for dating. The so-called 40-39 method is actually $^{40}$K-$^{40}$Ar dating but employing a somewhat different analytical technique for the potassium. The key is the production of $^{39}$Ar by a nuclear reaction on $^{39}$K, the most abundant of potassium’s three isotopes:

$^{39}$K (n,p) $^{39}$Ar

The reaction is produced by irradiating a sample with neutrons in a reactor. It is important to distinguish this reaction from simple neutron capture, but we can nevertheless define a reaction cross-sec-

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$^\dagger$ The Solver, an add-in tool that comes with Microsoft Excel™ can be used to solve problems such as this.
The amount of $^{39}$Ar produced is then a function of the amount of $^{39}$K present, the reaction cross-section, the neutron flux, and the irradiation time. Since the $^{40}$K/$^{39}$K ratio in the Earth is constant (at any given time), the amount of $^{40}$K can be calculated from $^{39}$Ar. In practice, the situation is more complex because the reaction cross-section is a function of neutron energy and there typically is a spectrum of energies present. The production of $^{39}$Ar from $^{39}$K can be expressed as:

$$^{39}\text{Ar} = ^{39}\text{K} \int \phi \sigma_e \, de$$  \hspace{1cm} (4.9)

where $e$ is the neutron energy, $\phi$ is the flux of neutrons with energy $e$, and $\sigma_e$ is the capture cross section for that energy, and $\tau$ is irradiation time. The $^{40}$Ar*/$^{39}$Ar is obtained by dividing equ. 4.3 by 4.9:

$$\frac{^{40}\text{Ar}^*}{^{39}\text{Ar}} = \frac{^{40}\text{K}(e^{\lambda \tau} - 1)}{^{39}\text{K} \int \phi \sigma_e \, de}$$  \hspace{1cm} (4.10)

In practice, the analysis is performed by simultaneously irradiating and analyzing a standard of known age. The flux, capture cross section, and decay constant terms will be the same for the standard as for the unknown sample. We can combine them into a single term, C, as:

$$C = \frac{1}{\lambda} \frac{\lambda}{\tau} \int \phi \sigma_e \, de$$  \hspace{1cm} (4.11)

and equation 4.9 becomes:

$$\frac{^{40}\text{Ar}^*}{^{39}\text{Ar}} = \frac{^{40}\text{K}(e^{\lambda \tau} - 1)}{^{39}\text{K}}$$  \hspace{1cm} (4.12)

The value of C can be determined from analysis of the standard, so that 4.12 can be solved for the age.

Another problem is the production of both $^{39}$Ar and $^{40}$Ar by other reactions that include $^{40}$K(n,p)$^{40}$Ar, $^{40}$Ca(n,α)$^{36}$Ar, and $^{40}$Ca(n,α)$^{36}$Ar. These must be corrected for. Generally, $^{37}$Ar, produced by $^{40}$Ca(n,α)$^{37}$Ar, is used to make these corrections.

In conventional K-Ar dating, Ar is released from samples by fusing in vacuum. However, we might guess from our knowledge of diffusion that a sample will begin to lose Ar before it reaches its melting temperature. If the ratio of radiogenic $^{40}$Ar to $^{39}$K (and therefore to $^{39}$Ar) were distributed uniformly throughout the sam-
Other Complications Affecting Lecture 4 within the mantle. Minerals crystallizing in the pre-ratios greater than the atmospheric ratio; this will lead to too old an age if not properly.

calculatively corrected for the presence of atmospheric Ar by measuring the Ar/Ar ratio. Atmospheric argon has a constant Ar/Ar ratio of 295.5. Only Ar present in excess of this ratio is considered radiogenic and used to calculate the Ar/Ar ratio. Nevertheless, some samples can have “initial” Ar/Ar ratios greater than the atmospheric ratio; this will lead to too old an age if not properly accounted for. It is this “excess” argon that is of greatest concern.

In the previous section, we saw two examples of Ar release spectra: one where there was only minor loss of Ar from the rims, and another where significant fractions of the total Ar had been lost due to metamorphic heating. Figure 4.4 showed spectra that almost perfectly match theoretical patterns for diffusional loss. Such examples are relatively rare; most spectra are more complex. For example, some samples that have been reheated show false plateaus that correspond to ages intermediate between the crystallization age and the reheating age. An additional problem in interpreting such spectra is that samples that have not been subjected to reheating events but cooled slowly originally can show release spectra that mimic those of reheated samples in Figure 4.4.

Recoil of Ar produced by the K(n,p)Ar reaction during irradiation can also produce problems. The recoil results in loss of Ar from sites near the mineral surface. For large grains, this is largely insignificant, but for small grains, this can lead to significant Ar loss, leading in turn to erroneously old apparent ages.

In most cases, the Ar present in a sample will not be pure radiogenically produced Ar. Non-radiogenic argon is often called excess Ar. Ar ratios used to calculate ages in release spectra are typically corrected for the presence of atmospheric Ar by measuring the Ar/Ar ratio. Atmospheric argon has a constant Ar/Ar ratio of 295.5. Only Ar present in excess of this ratio is considered radiogenic and used to calculate the Ar/Ar ratio. Nevertheless, some samples can have “initial” Ar/Ar ratios greater than the atmospheric ratio; this will lead to too old an age if not properly accounted for. It is this “excess” argon that is of greatest concern.

Excess Ar can have two sources. First, it can arise when minerals crystallize under a finite partial pressure of Ar. For example, mantle-derived basalts have been shown in some cases to have initial Ar/Ar ratios of up to 40,000. The high Ar/Ar ratio reflects production of Ar by decay of K within the mantle. Minerals crystallizing in the presence of this gas will trap some of this Ar, which
will result an anomalously old age upon analysis. This is referred to as inherited Ar. Second, during a thermal event, $^{40}$Ar diffusing out of some minerals may be taken up by other minerals. Since this $^{40}$Ar is diffusing into the mineral grain, its concentration will be highest in the exterior of grains and thus will tend to be released at the lowest temperatures. An example is shown in Figure 4.5.

When excess Ar is held in more than one crystallographic site, for example different minerals in the analyzed sample, release spectra can reveal a saddle shape. An example is shown in Figure 4.6. This sample is a calcic plagioclase from Broken Hill in Australia. The true metamorphic age is approximately 1600 Ma. Even the minimum values in the bottom of the saddle are too old. Electron microscopy of the plagioclase revealed that it had evolved into a Ca-rich and Na-rich plagioclase. The saddle shape results because Ar in one of the phases diffuses readily and is thus released at low temperature, and diffuses more slowly in the other, resulting in release at high temperature.

**$^{40}$Ar-$^{39}$Ar Isochrons**

The data from various temperature release steps are essentially independent observations of Ar isotopic composition. Because of this, they can be treated much the same as in conventional isochron treatment. The isochron equation, written for the K-Ar system is:

$$
\frac{^{40}\text{Ar}}{^{36}\text{Ar}} = \left( \frac{^{40}\text{Ar}}{^{36}\text{Ar}} \right)_0 + \frac{^{40}\text{K}}{^{36}\text{Ar}} (e^{4.13t} - 1)
$$

When $^{40}$Ar/$^{36}$Ar data from a series of samples are plotted against $^{40}$K/$^{36}$Ar, the slope of the resulting line will be proportional to age, and the intercept gives the initial $^{40}$Ar/$^{36}$Ar ratio. Since

![Figure 4.5. Ar release spectrum of a hornblende in a Paleozoic gabbro reheated in the Cretaceous by the intrusion of a granite. Anomalously old apparent ages in the lowest temperature release fraction results from diffusion of radiogenic Ar into the hornblende during the Cretaceous reheating. From McDougall and Harrison (1988).](image)

![Figure 4.6. Ar release spectrum from a calcic plagioclase from Broken Hill, Australia. Low temperature and high temperature fractions both show erroneously old ages. This peculiar saddle shaped pattern, which is common in samples containing excess Ar, results from the excess Ar being held in two different lattice sites. From McDougall and Harrison (1988).](image)
for all release fractions of a sample the efficiency of production of \(^{39}\text{Ar}\) from \(^{39}\text{K}\) is the same and \(^{40}\text{K}/^{39}\text{K}\) ratios are constant, we may substitute C\(^{39}\text{Ar}\) for \(^{40}\text{K}\):

\[
\frac{^{40}\text{Ar}}{^{36}\text{Ar}} = \left( \frac{^{40}\text{Ar}}{^{36}\text{Ar}} \right)_0 + \frac{^{39}\text{Ar}}{^{36}\text{Ar}} c(e^{\lambda t} - 1)
\]

C is a constant that depends on the efficiency of \(^{39}\text{Ar}\) production during irradiation. Thus when \(^{40}\text{Ar}/^{36}\text{Ar}\) ratios from a series of release fractions are plotted against \(^{39}\text{Ar}/^{40}\text{Ar}\), the slope of the resulting line will be proportional to the age of the sample, as is illustrated in Figure 4.7.

The use of the isochron diagram can help to identify excess Ar and its nature (e.g., atmospheric, inherited, etc.). It also provides a crucial test of whether ages obtained in release spectra are meaningful or not. A drawback of this diagram is that \(^{36}\text{Ar}\), which is the denominator in both the ordinate and abscissa, is often present in only trace amounts and is difficult to measure precisely. Because it appears in both ordinate and abscissa, errors in its measurements can produce correlations that imitate isochrons.

An alternative is to use a plot of \(^{36}\text{Ar}/^{40}\text{Ar}\) against \(^{39}\text{Ar}/^{40}\text{Ar}\) (Figure 4.8), often called an inverse isochron plot. We can think of the Ar in a sample as a mixture of a trapped component and a radiogenic component. As such, the data for various release fractions should plot as a straight line on such a plot. The radiogenic component has a \(^{36}\text{Ar}/^{40}\text{Ar}\) ratio of 0 (because \(^{36}\text{Ar}\) is not produced by radioactive decay), whereas the trapped, non-radiogenic component can be found by extrapolating to a \(^{39}\text{Ar}/^{40}\text{Ar}\) ratio of 0 (corresponding to a \(^{39}\text{K}/^{40}\text{Ar}\) ratio of 0; since \(^{39}\text{K}\) is proportional to \(^{40}\text{K}\), this also corresponds to a \(^{40}\text{K}/^{40}\text{Ar}\) ratio of 0). Thus the age may be computed from the \(^{39}\text{Ar}/^{40}\text{Ar}\) ratio obtained by extrapolating the correlation line to \(^{36}\text{Ar}/^{40}\text{Ar}\) to 0, and the composition of the trapped component by extrapolating to \(^{39}\text{Ar}/^{40}\text{Ar}\) of 0.

Figure 4.9 provides an example of how the inverse isochron plot may be used to identify trapped components. The original release data showed a disturbed pattern and lacked a plateau (not shown). The inverse isochron plot (Figure 4.9a) revealed two correlations suggesting the presence of two distinct trapped components. The lower intercept yielded an age of 149.1 Ma. When the data were corrected for the trapped component and replotted on a release spectrum, they produced a plateau corresponding to the same age as the isochron age.
Figure 4.9. (a) Inverse isochron diagram revealing the presence of two excess Ar components. (b) Ar release spectrum for the same sample after correction for non-atmospheric excess Ar.

REFERENCES AND SUGGESTIONS FOR FURTHER READING


