Geol. 655 Isotope Geochemistry

lecture 5 Spring 2003

GEOCHRONOLOGY I

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. However, except for some special aspects of K-Ar and U-Th-Pb, geochronology with one system does not differ much in principle from other systems.

THE K-AR-CA SYSTEM

Two aspects of this system make it special. First, it is a branched decay: a ^{40}K nucleus (an odd-odd) may decay to either a ^{40}Ca by β^- 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:

$$R = \frac{\lambda_e}{\lambda_\beta} \qquad 5.1$$

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:

$$\lambda = \lambda_\beta + \lambda_e = 5.543 \times 10^{-10}\ \text{yr}^{-1} \qquad 5.2$$

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 4.7) becomes:

$$^{40}\text{Ar}^* = \frac{\lambda_e}{\lambda}\ ^{40}\text{K}(e^{\lambda t} - 1) \qquad 5.3$$

where the asterisk indicates radiogenic ^{40}Ar. Note we can write a similar equation for ^{40}Ca* by substituting λ_β for λ_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 in 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 diffi-

culty 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, though not always, do so with very little Ar. A good example of an exception is pillow basalts formed on the seafloor. 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 5.3 to solve for it by measuring the ^{40}K and ^{40}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. This atmospheric Ar is readily corrected for since the atmospheric ratio of $^{40}Ar/^{36}Ar$ is known to be 295.5. By measuring the amount of ^{36}Ar present, we can deduce the amount of atmospheric ^{40}Ar initially present. Our age equation (equation 4.17) becomes simply:

$$\frac{^{40}Ar}{^{36}Ar} = 295.5 + \frac{\lambda_e}{\lambda}\frac{^{40}K}{^{36}Ar}(e^{\lambda t} - 1) \qquad 5.4$$

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 $^{40}Ar/^{36}Ar$ ratio.

Diffusion

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:

$$D = D_o e^{-E_A/RT} \qquad 5.5$$

where D is the diffusion coefficient, D_o 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 then related to the concentration gradient by:

$$J = -D\frac{\partial C}{\partial x} \qquad 5.6$$

where C is the concentration and x is distance. Figure 5.1 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 flux, or diffusion rate. Using the values of E_A and D_o 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. For a temperature of 300 K (27°C), D would be 4×10^{-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 is lost from biotites of 97μ radius in 2-3 weeks (you can understand then why the experiments were done at these temperatures and not lower ones).

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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).

$$f = \frac{4}{\pi^{1/2}}\left(\frac{Dt}{a^2}\right)^{1/2} - \frac{Dt}{a^2} - \frac{1}{3\pi^{1/2}}\left(\frac{Dt}{a^2}\right)^{3/2} \qquad 5.7$$

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 5.1. Figure 5.2 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 5.4 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 has derived an equation for 'closure temperature' that considers cooling rate as well as diffusion rate.

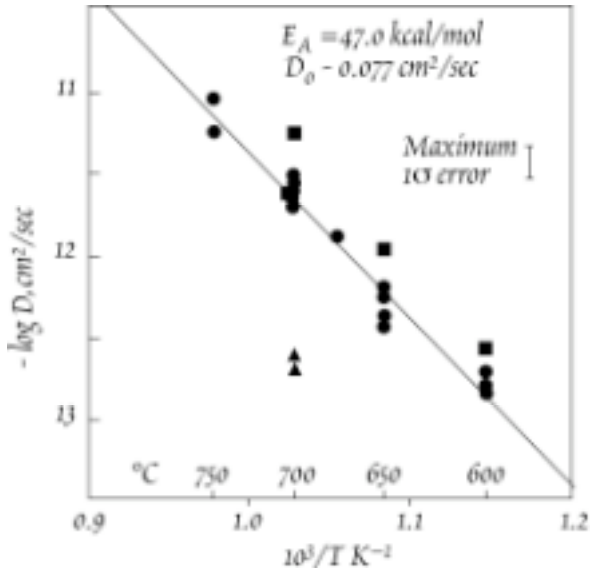


Figure 5.1 Log of the diffusion coefficient for argon in biotite against the inverse of thermodynamic temperature. Circles and squares indicate different size fractions of biotite used in 1 kbar experiments. Triangles are 14 kbar experiments. From Harrison et al. (1985).

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 loosing 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

* Note that this equation implies that diffusional loss will be inversely related to crystal size: larger crystals will lose less.

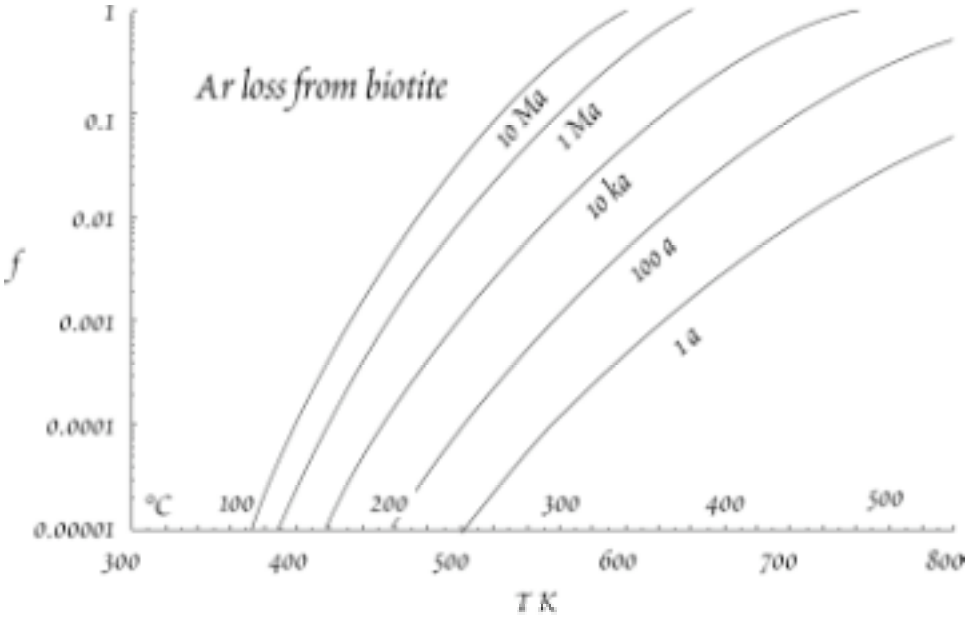


Figure 5.2. Fraction of Ar lost from a 150 μ cylindrical crystal as a function of temperature for various heating times. All Ar is lost in 10 Ma at 300°C, or in 1 Ma at 360° C.

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:

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

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-section. 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 are typically a spectrum of energies present. The production of ^{39}Ar from ^{29}K can be expressed as:

$$^{39}\mathrm{Ar} = {}^{39}\mathrm{K} \int \phi_e \sigma_e \, de \qquad 5.8$$

where e is the neutron energy, ϕ_e is the flux of neutrons with energy e, and σ_e is the capture cross section for that energy, and t is irradiation time. The ^{40}Ar*/^{39}Ar is then:

$$\frac{^{40}\mathrm{Ar}^*}{^{39}\mathrm{Ar}} = \frac{\lambda_e}{\lambda} \frac{^{40}\mathrm{K}(e^{\lambda t} - 1)}{^{39}\mathrm{K} \int \phi_e \sigma_e \, de} \qquad 5.9$$

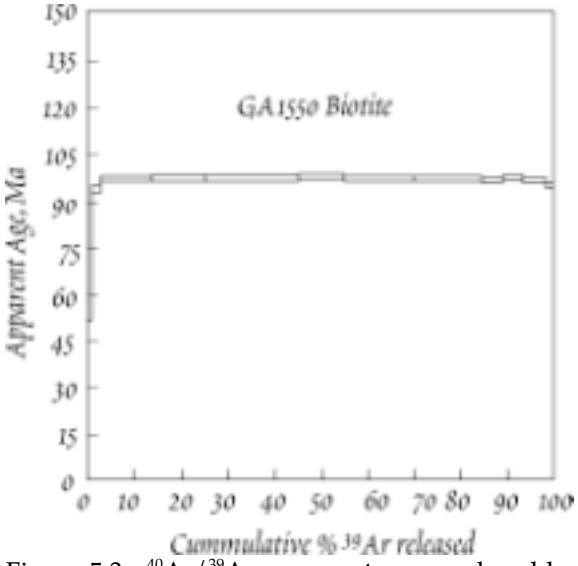


Figure 5.3. $^{40}Ar/^{39}Ar$ age spectrum produced by step heating of a biotite from a granitic gneiss. From McDougall and Harrision (1988).

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:

$$C = \frac{\lambda_e}{\phi \int \sigma_e \lambda_e de} \qquad 5.10$$

and equation 5.9 becomes:

$$\frac{^{40}Ar^*}{^{39}Ar} = C\frac{^{40}K(e^{\lambda t} - 1)}{^{39}K} \qquad 5.11$$

The value of C can be determined from analysis of the standard, so that 5.11 can be solved for the age.

Another problem is the production of both ^{39}Ar and ^{40}Ar by other reactions that include $^{40}K(n,p)^{40}Ar$, $^{40}Ca(n,n\alpha)^{36}Ar$, and $^{42}Ca(n,\alpha)^{39}Ar$. These must be corrected for. Generally, ^{37}Ar, produced by $^{40}Ca(n, \alpha)^{37}Ar$, 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 K (and therefore to ^{39}Ar) were distributed uniformly throughout the sample, a sample of gas taken before the sample fused would produce the same age as for total fusion. We might guess, however, that some parts of the crystal have preferentially lost Ar through diffusion during the initial cooling of the crystal, or perhaps during some subsequent reheating event. Since the diffusion rate is proportional to the concentration gradient, we can anticipate that diffusion will be faster from the rims of crystals where the concentration gradient is higher than in the interior of crystals. So we might expect crystal rims to experience Ar loss at lower temperatures than crystal interiors. The rims would then record younger ages. As we heat the sample, we would also expect rims to start to give up there Ar at the lowest temperatures, partly for this reason, and partly because the Ar has less distance to go to get out. The lower $^{40}Ar/^{39}Ar$ of the gas in the rim would be seen as a lower age (which may or may not have significance). As we increased the temperature, the more retentive parts of the crystal would release their gas, and we could expect the

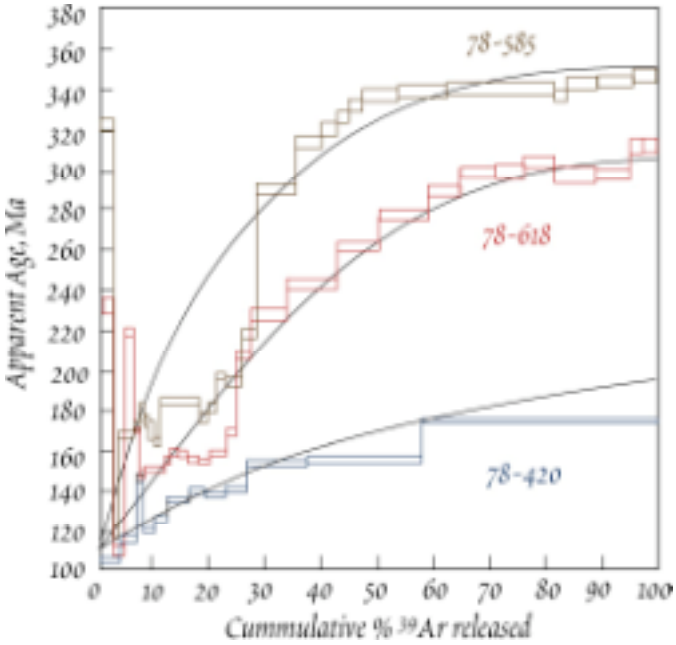


Figure 5.4 . Ar release spectra for hornblendes taken from varying distance from a 114 million year old intrusion. The crystallization age of the samples is 367 Ma. Curves show calculated release spectra expected for samples that lost 31, 57, and 78% of their argon. From McDougall and Harrison, 1988.

$^{40}Ar/^{39}Ar$ and the apparent age to increase. If some parts of the crystals have lost no gas, their $^{40}Ar/^{39}Ar$ ratios would record the 'correct' age, even though the crystal as a whole has suffered some loss. Figure 5.3 is an Ar release diagram for a biotite exhibiting this sort of behavior. Conventional K-Ar dating would have produced an age intermediate between the 'correct' age and the apparent young age of those parts of crystal that have suffered loss of radiogenic ^{40}Ar. Thus the combination of the $^{40}Ar/^{39}Ar$ method with step-heating provides a means of retrieving useful geochronological information from samples whose value would have otherwise been compromised because of diffusional loss. In a certain sense, we are relaxing our requirement that the system must have remained closed: with $^{40}Ar/^{39}Ar$ dating, we require only that some part of the system have remained closed.

Most Ar release spectra are not so simple as that in Figure 5.3. Figure 5.4 shows Ar release spectra for a series of hornblende samples taken at varying distances from the contact with an intrusive granodiorite. All show significant Ar loss as a result of heating from the intrusion. None retain, even at the highest release temperature, the true age of 367 Ma.

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