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## A Theory of “Real” K-Ar Clocks

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### ABSTRACT

A good approximation to diffusional losses in minerals can be obtained by use of the concept of an escape constant:

$$\lambda_d = \frac{g D}{x^2}$$

where  $g$  is the geometry factor,  $D$  is the diffusion coefficient and  $x$  is the pertinent diffusion coefficient. The escape constant is conceptually simple and analogous to the radioactive decay constant. In this way,  $^{40}\text{Ar}$  can be treated as if it were a radioactive (escaping) daughter product of  $^{40}\text{K}$ . The use of a geometry factor is similar to the use of activity coefficients to preserve the simplicity of mass action equations.

By use of the escape constant concept, a theory of “real” K-Ar clocks can be developed. The “real” K-Ar clock is treated as a more or less open system in the presence of an external environment containing a significant partial pressure of  $^{40}\text{Ar}$ . The equation of the “ideal” K-Ar clock is one of five special cases which can be derived from the more general equation of the “real” K-Ar clock.

### “Ideal” K-Ar Clocks

Simple ideal conditions are usually assumed for K-Ar dating. That is, the following assumptions are tacitly accepted:

1. At a time  $t = 0$ , the K-Ar geochronometer contains no  $^{40}\text{Ar}$ .
2. Following the time  $t = 0$ , the K-Ar clock remains a closed system accumulating  $^{40}\text{Ar}$  from  $^{40}\text{K}$  by radioactive decay alone.

$^{40}\text{K}$  decays to  $^{40}\text{Ar}$  by electron capture at a rate  $\lambda_K$  and to  $^{40}\text{Ca}$  at rate  $\lambda_\beta$ . The total rate of decay  $\lambda$  is equal to the sum of the separate decay rates:

$$\lambda = \lambda_\beta + \lambda_K = \frac{0.693}{T_{1/2}} \quad (1)$$

The fraction of  $^{40}\text{K}$  decaying to  $^{40}\text{Ar}$  is

$$\frac{{}^{40}\text{Ar}}{{}^{40}\text{Ar} + {}^{40}\text{Ca}} = \frac{\lambda_K}{\lambda_K + \lambda_\beta} = \frac{\lambda_K}{\lambda} \quad (2)$$

The amount of  $^{40}\text{Ar}$  accumulated in time  $t$  is

$${}^{40}\text{Ar} = \frac{\lambda_K}{\lambda} ({}^{40}\text{K}_t - {}^{40}\text{K}) \quad (3)$$

i.e., it is equal to the total  $^{40}\text{K}$  transmuted, which is the amount at time  $t$ ,  $^{40}\text{K}_t$ , minus the amount at present,  $^{40}\text{K}$ , times the fraction decaying to  $^{40}\text{Ar}$ , i.e.,  $\lambda_K/\lambda$ . But

$$^{40}\text{K}_t = ^{40}\text{K} \exp(\lambda t) \quad (4)$$

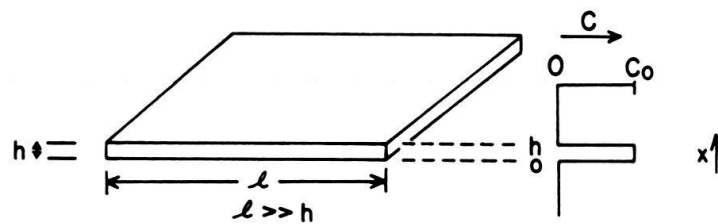
and also substituting in equation (3)

$$^{40}\text{Ar} = \frac{\lambda_K}{\lambda} ^{40}\text{K} \{ \exp(\lambda t) - 1 \} \quad (5)$$

What is the time  $t$ ? It is the time required to generate the measured amount of argon from the measured amount of potassium.

### Diffusion from minerals

However, at elevated temperatures the K-Ar clock is not a closed system. Also, in the intrusive environment it is in the presence of volatiles including  $^{40}\text{Ar}$ . Depending upon the solubility of argon in the mineral and the external pressure, argon can leak in or out. In order to determine the rate of leak exactly, it is necessary to specify the diffusion coefficient ( $D$ ) and the geometry of the mineral. Unfortunately, real minerals do not exactly fit ideal geometric models. The study of the mica, phlogopite, by EVERNDEN et al. (1960) provides a good example to illustrate this point. These workers found that no single ideal model would provide a best fit for the data over the entire range of temperature through which phlogopite is stable. A slab model seemed to fit the data best below  $500^\circ\text{C}$  and above  $800^\circ\text{C}$ , but between these temperatures a cylindrical model provided the best fit. In general, diffusion models are useful conveniences providing more or less good approximations to reality. In some cases, rigorous adherence to ideal models may obscure significant relationships which otherwise might become apparent.



$$C = C_0 \text{ for } 0 < x < h \text{ at } t = 0$$

$$C = 0 \text{ for } x = 0 \text{ and } x = h \text{ at } t > 0$$

Fig. 1. Slab model for diffusion (for derivation of equations see JOST, 1960, p. 39-42).

The slab model used by EVERNDEN and CURTIS (op. cit.) is shown in Figure 1. The equation for the average concentration within the slab of the diffusing component (e.g., argon),  $\bar{c}$  as a function of time,  $t$ , is given by the following equation (JOST, 1960, p. 39-42):

$$\bar{c} = \frac{c_0}{h} \int_0^h (c/c_0) dx = \frac{8c_0}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp(-\{2n+1\}^2 y) \quad (6)$$

where  $y = D\pi^2 t/h^2$ . This equation is plotted for two values of  $D/h^2$  in Figure 2. These two values represent a change of about  $75^\circ\text{C}$  in temperature.

When  $t$  is sufficiently large, the first term in the series gives a good approximation:

$$\bar{c} = \frac{8c_0}{\pi^2} \exp(-t/\tau) \quad (7)$$

where  $\tau = t/y = h^2/\pi^2 D$ .

This equation represents an exponential decay of a "virtual" initial concentration,  $8c_0/\pi^2$ . It provides, for all practical purposes, an exact solution for the last  $2/3$  of argon loss.

In this case, we may define an escape constant,  $\lambda_d$ , as follows:

$$\lambda_d = \frac{1}{\tau} = \frac{\pi^2 D}{h^2} \quad (8)$$

and, in general,

$$\lambda_d = \frac{gD}{x^2} \quad (9)$$

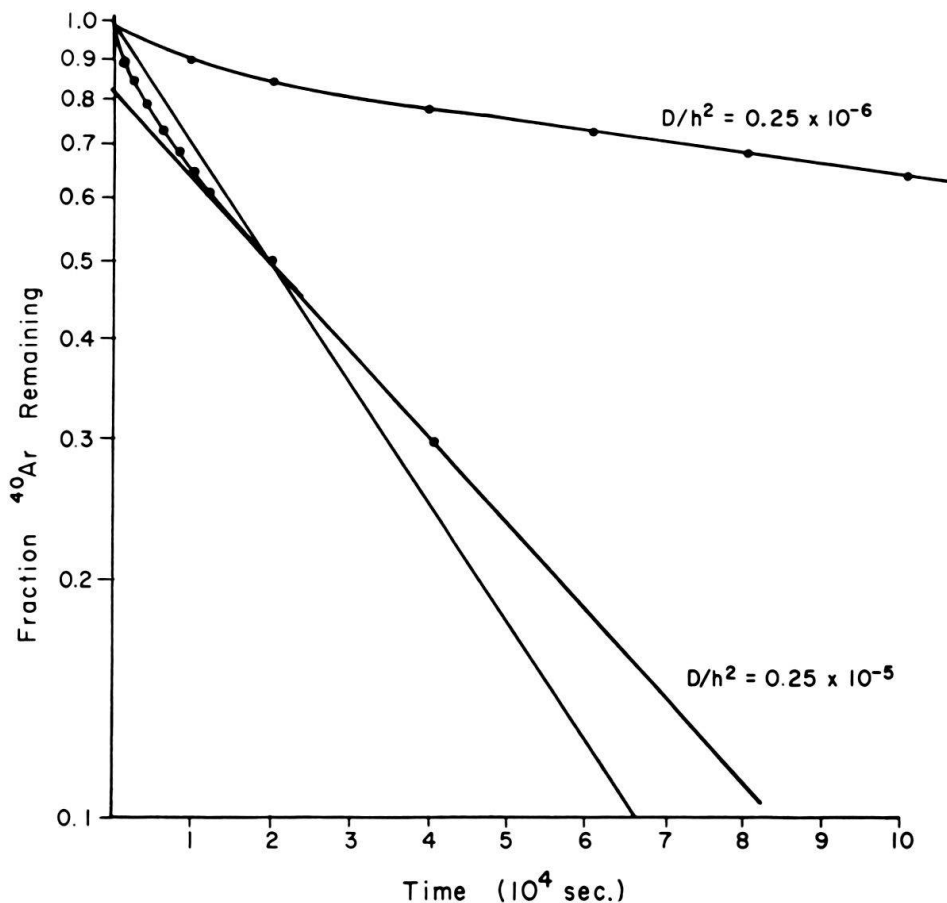


Fig. 2. Fraction of argon remaining in a slab according to rigorous solution and exponential approximations. The two diffusion curves represent a temperature difference of about  $75^\circ\text{C}$ . The error in using the exponential approximation is equivalent to a temperature difference of not more than approximately  $10^\circ\text{C}$ . The  $D/h^2$  curves were calculated by LAUGHLIN (1969).

where  $x$  is the pertinent diffusion coefficient and  $g$  is the geometry factor which is equal to  $\pi^2$  in the above case and also for spherical geometry under the same circumstances, i.e., for large  $t$  (for a cylinder of infinite length,  $g$  is equal to  $(2.405)^2$ ).

We can also approximate equation (6) by an exponential decay with a real initial concentration,  $c_0$ :

$$\bar{c} = c_0 \exp(-\lambda_d t) \quad (10)$$

Recalling that  $\lambda_d = 0.693/(T_{1/2})_D$ , we can solve equation (10) for  $\lambda_d$  when  $c_0/\bar{c} = 2$ , i.e., at  $t = (T_{1/2})_D$  which is the time required for diffusional loss of half of the initial concentration. This can also be done for the sphere and cylinder:

$$\lambda_d = 14.2 \frac{D}{h^2} \quad (\text{slab}) \quad (11a)$$

$$\lambda'_d = 12.5 \frac{D'}{r_c^2} \quad (\text{cylinder}) \quad (11b)$$

$$\lambda''_d = 35.7 \frac{D''}{r_s^2} \quad (\text{sphere}). \quad (11c)$$

This exponential approximation will underestimate losses of less than 50% and overestimate losses greater than 50% as shown in Figure 2. The inaccuracy introduced is equivalent to an uncertainty of no more than  $\pm 10^\circ\text{C}$  in temperature. However, when one considers that the assumed geometry for a mineral seldom represents rigorously the actual geometry and the uncertainties with respect to temperature of natural environments, etc., equations (10) and (11) provide an adequate approximation for both large and small losses.

For large losses, equation (7) with the appropriate geometry factor is preferred. In general, for any given fractional loss, some value of  $g$  in equation (9) will represent an adequate approximation and allow the use of the concept of an escape constant,  $\lambda_d$ , which is conceptually simple and analogous to the radioactive decay constant  $\lambda$ . This approach is similar to the use of activity coefficients to preserve the simplicity of mass action equations.

### Solubility of argon in minerals

The presence of measurable excess environmental argon in minerals from the intrusive environment is a fairly ubiquitous phenomenon (see DAMON, 1968, for extended discussion and review). Several Russian workers have performed laboratory experiments in which they have demonstrated the adsorption of argon by minerals. The work of GERLING et al. (1965) was, perhaps, the most thorough. They measured the adsorption of argon by a number of minerals at 100 bars argon pressure and around  $1000^\circ\text{C}$ . The amount adsorbed ranged from about  $2.5 \times 10^{-7}$  m/g to about  $2.5 \times 10^{-6}$  m/g.

A. W. LAUGHLIN (1969), while working in this laboratory, performed argon introduction and diffusion experiments on albite. He found that significant quantities

of argon can be introduced into albite at high temperature (1000°C) even at argon pressures as low as 1 bar. LAUGHLIN used his data to evaluate the maximum concentration ( $S^*$ ) of argon in albite using the following equation:

$$S = \frac{S^*bp}{1 + bp} \quad (12)$$

where  $S$  = concentration of dissolved argon,

$p$  = partial pressure of argon,

$b = c \exp(-E/k\theta)$ .

The relationship held fairly well up to several kilobars of argon pressure and, thus, the parameters of the equation could be evaluated ( $S^* = 1.44 \times 10^{-5}$  m/g,  $b = 2.7 \times 10^{-4}$  bars<sup>-1</sup>). At low values of  $bp$  this equation reduces to Henry's Law and, consequently, a value of  $S = 3.9 \times 10^{-10}$  m/g is predicted at 0.1 bar. Measurements of excess argon in plagioclase from intrusive igneous rocks suggest that the <sup>40</sup>Ar pressure seldom exceeds this amount and, typically, it is an order of magnitude lower or about equal to the partial pressure of argon in the earth's atmosphere.

### "Real" K-Ar Clocks

The "real" K-Ar clock must be treated as an open system in the presence of an external environment containing a significant partial pressure of <sup>40</sup>Ar. For this case, we may write the following differential equation:

$$\frac{d^{40}\text{Ar}}{dt} = \lambda_K^{40}\text{K} - \lambda_d(^{40}\text{Ar} - S^*b^{40}\text{P}) \quad (13)$$

i.e., the rate of change of the <sup>40</sup>Ar content is equal to the increment due to decay, minus or plus the leak in or out depending on whether the mineral is subsaturated or supersaturated with argon. The saturation value,  $S^*b^{40}\text{P}$ , assumes the validity of Henry's Law at least under a limited set of conditions. Integrating, we get the following general equation for net argon accumulation:

$$\begin{aligned} ^{40}\text{Ar} = & ^{40}\text{Ar}_0 \exp(-\lambda_d t) + ^{40}\text{K} \frac{\lambda_K}{(\lambda - \lambda_d)} \{ \exp(\lambda - \lambda_d)t - 1 \} \\ & + S^*b^{40}\text{P} \{ 1 - \exp(-\lambda_d t) \} \end{aligned} \quad (14)$$

The first term represents the decay of any initial argon already present at the time of elevation to temperature  $\theta$ , i.e.,  $t = 0$ . The second term is equivalent to equation (5) representing the accumulation due to radioactive decay modified for leakage. The effective decay rate is now  $(\lambda - \lambda_d)$  rather than  $\lambda$  as in equation (5). The last term represents the inward diffusion of <sup>40</sup>Ar from the external environment.

When the temperature ( $\theta$ ) is sufficiently high, a steady state is attained, i.e., there is no net gain or loss of <sup>40</sup>Ar:

$$\frac{d^{40}\text{Ar}}{dt} = 0 = \lambda_K^{40}\text{K} - \lambda_d^{40}\text{Ar} + \lambda_d S^*b^{40}\text{P} \quad (15)$$

Solving for  $^{40}\text{Ar}$ ,

$$^{40}\text{Ar} = \frac{\lambda_K}{\lambda_d} ^{40}\text{K} + S^*b ^{40}\text{P} \quad (16)$$

At magmatic temperatures  $\lambda_d \gg \lambda_K$  and,

$$^{40}\text{Ar} = S^*b ^{40}\text{P} \quad (17)$$

However, at high grade metamorphic temperatures between 400 to 500°C, there will be two components of  $^{40}\text{Ar}$  as given by equation (16): a transient component given by  $\lambda_K/\lambda_d$   $^{40}\text{K}$  and a dissolved environmental excess component,  $S^*b$   $^{40}\text{P}$ . At a lower temperature,  $\theta$ , when the leak rate  $\lambda_d$  is approximately equal to or less than the decay rate  $\lambda$ , the  $^{40}\text{Ar}$  content of the mineral becomes a function of time and equation (16) is no longer applicable. At such temperatures, the time-dependent equation (14) is applicable. As the temperature is lowered further, equation (14) for the “real” clock reduces to that for the “ideal” clock, equation (5), which is a special case of equation (14).

### Components of argon

To avoid semantic difficulties, it may be well to define certain components of  $^{40}\text{Ar}$  which may affect atomic clock readings:

- |  |   |
|--|---|
| I. Environmental $^{40}\text{Ar}$ :        | $^{40}\text{Ar}$ in the environment external to the reference mineral.  |
| II. Radiogenic $^{40}\text{Ar}$ :          | $^{40}\text{Ar}$ produced by radioactive decay in a potassic reference mineral which is the atomic clock under consideration.   |
| III. Extraneous $^{40}\text{Ar}$ :         | Any $^{40}\text{Ar}$ contained within a mineral separate other than the radiogenic components accumulated after a time, $t = 0$ , defined by a thermal or chemical event. |
| A. Transient $^{40}\text{Ar}$ :            | $^{40}\text{Ar}$ produced in the reference mineral under transient conditions prior to time, $t = 0$ .  |
| B. Inherited $^{40}\text{Ar}$ :            | $^{40}\text{Ar}$ inherited from a previous set of environmental conditions prior to time, $t = 0$ , excluding the transient $^{40}\text{Ar}$ .                            |
| C. Nucleogenic Argon:                      | Argon produced by particle reactions.   |
| D. Environmental Excess $^{40}\text{Ar}$ : | $^{40}\text{Ar}$ dissolved in the reference mineral as a result of an external environmental $^{40}\text{Ar}$ pressure (other than the atmosphere).                       |
| E. Atmospheric Contamination:              | $^{40}\text{Ar}$ accompanied by $^{36}\text{Ar}$ adsorbed from the atmosphere.  |
| F. Xenolithic $^{40}\text{Ar}$ :           | $^{40}\text{Ar}$ inherited from xenolithic contamination at elevated temperature.   |
| G. Radiogenic Contamination:               | Foreign material containing $^{40}\text{Ar}$ contaminating the sample either in the field or laboratory during ambient surface conditions.                                |

In order to interpret a K-Ar date, we need a point of reference. This is the time,  $t = 0$ , defined by a thermal or chemical event. All argon accumulated in the sample other than the radiogenic argon accumulated following the event at  $t = 0$  is extraneous.

Can we distinguish these different components of argon? The answer is, yes, in many cases. Xenolithic and other contamination components can usually be detected by microscopic examination. Atmospheric and nucleogenic argon are signaled by the argon isotopic composition. Environmental excess argon can be detected by analyzing nonpotassic minerals. The transient component is dependent on  $^{40}\text{K}$  and  $\lambda_d$  whereas the environmental excess, at steady state, is not.

### Concluding remarks

As the environmental conditions are changed, the “real” K-Ar clock will continuously respond to its changed environment. However, we may abstract certain cases which are of particular interest:

- Case 1.  $\lambda \gg \lambda_d$ : The equations reduce to that for the ideal clock (equation 5).
- Case 2.  $\lambda > \lambda_d$ : Argon will accumulate with an apparent decay rate of  $(\lambda - \lambda_d)$  (equation 14).
- Case 3.  $\lambda_d > \lambda$ : A steady state is eventually attained, at which time the argon content is a function of temperature and the external partial  $^{40}\text{Ar}$  pressure:

$$^{40}\text{Ar} = \frac{\lambda_{\text{K}} \text{ } ^{40}\text{K}}{(\lambda_d - \lambda)} + S^*b \text{ } ^{40}\text{P} \quad (18)$$

- Case 4.  $\lambda_d \gg \lambda$ : A steady state is more or less rapidly attained dependent upon temperature, at which time the  $^{40}\text{Ar}$  content of the mineral is given by equation (16).
- Case 5.  $\lambda_d \gg \lambda_{\text{K}}$ : Transient  $^{40}\text{Ar}$  is negligible. Virtually all of the clock’s  $^{40}\text{Ar}$  content is environmental excess  $^{40}\text{Ar}$  (equation 17).

As a rough generalization, appealing to published diffusion data for minerals (FECHTIG and KALBITZER, 1966), the different cases correspond to the following geologic environments:

- Case 1. Ambient conditions near the earth’s surface.
- Case 2. Diagenesis and low grade metamorphism at temperatures of between  $50^\circ\text{C}$  to  $250^\circ\text{C}$  depending upon the diffusional properties of the mineral.
- Case 3. Low and medium grade metamorphism at temperatures of  $150^\circ\text{C}$  to  $350^\circ\text{C}$  depending upon the diffusional properties of the minerals.
- Case 4. Medium to high grade metamorphism or ultra-metamorphism – as the temperature increases the  $^{40}\text{Ar}$  content of the mineral is increasingly dependent solely upon the external partial pressure of  $^{40}\text{Ar}$ .
- Case 5. Basaltic magma – only the environmental excess component is significant.



With increased knowledge of the physical properties of K-Ar clocks, they will become useful indicators of the cooling history and the environmental conditions during metamorphism.

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