Fig. 9.1. Decay modes and energy levels for the radioactive isotope $^{40}\text{K}$. The electron capture (EC) mode to an excited state of $^{40}\text{Ar}$ reduces the energy by 0.05 MeV, followed by emission of a 1.46 MeV gamma ray to the ground state of $^{40}\text{Ar}$.
\[ 40\text{Ar}_{\text{total}} = 40\text{Ar}_I + \frac{\lambda_{\text{EC}}}{\lambda_{\text{total}}} 40\text{K}(e^{\lambda_{\text{total}}t} - 1) \]

\[ 40\text{Ar}^* = \left(\frac{\lambda_{\text{EC}}}{\lambda_{\text{total}}}\right) 40\text{K}(e^{\lambda_{\text{total}}t} - 1) \]

\[ t = \frac{1}{\lambda_{\text{total}}} \ln\left(\frac{40\text{Ar}^*}{40\text{K}} \frac{\lambda_{\text{total}}}{\lambda_{\text{EC}}} + 1\right) \]

---

**Fig. 10.1.** Schematic diagram of an argon extraction line coupled to a static gas mass spectrometer. After Dalrymple and Lanphere (1969).
\[ 40\text{Ar}^* = 40\text{Ar}_{\text{tot}} - 36\text{Ar} \left( \frac{40\text{Ar}}{36\text{Ar}} \right)_{\text{air}} - \left[ 38\text{Ar} \left( \frac{40\text{Ar}}{38\text{Ar}} \right)_{\text{spk}} \right] \]

\[ \left( \frac{40\text{Ar}}{36\text{Ar}} \right)_{\text{air}} = 298.7 \pm 0.1 \]

(used to be 295.5)

Fig. 10.2. Schematic argon isotope mass spectrum, showing fractions of each peak due to radiogenic Ar (white), spike (stippled) and atmospheric contamination (hatched). Size fractions are not shown to scale. After Dalrymple and Lanphere (1969).

Fig. 10.3. Error magnification in K–Ar dating (y axis) resulting from atmospheric argon contamination. Curves are calculated for 0.5%, 1%, 2% and 5% errors in the measurement of \(^{36}\text{Ar}\). After Cox and Dalrymple (1967).
Fig. 10.4. Contents of (excess) radiogenic $^{40}$Ar in submarine pillows from Hawaii, plotted against inward distance from the pillow rim. Apparent K–Ar ages for each sample are noted in Myr. After Dalrymple and Moore (1968).
\[
\left( \frac{^{40} \text{Ar}}{^{36} \text{Ar}} \right)_{\text{total}} = \left( \frac{^{40} \text{Ar}}{^{36} \text{Ar}} \right)_{\text{atm+excess}} \\
+ \frac{^{40} \text{K}}{^{36} \text{Ar}} \frac{\lambda_{EC}}{\lambda_{EC} + \lambda_{\beta}} (e^{\lambda_{\text{total}}t} - 1)
\]

5 salt samples combined
- fit to stepped-release data
- Open symbols: SDS-5, SDS-6, SDS-7, SDS-8, SDS-9
- Stepped release symbols
- Filled symbols: total release

Age = 256.5 Ma
\[
(\frac{^{40} \text{Ar}}{^{36} \text{Ar}})_o = 294.2
\]
\[
\left( \frac{^{40}\text{Ar}}{^{36}\text{Ar}} \right)_{\text{total}} = \left( \frac{^{40}\text{Ar}}{^{36}\text{Ar}} \right)_{\text{atm+excess}} + \frac{^{40}\text{K}}{^{36}\text{Ar}} \frac{\lambda_{EC}}{\lambda_{EC} + \lambda_{\beta}} (e^{\lambda_{\text{total}}t} - 1)
\]

Fig. 10.5. K–Ar isochron plot for a lava of historical age from Mount Wellington, New Zealand, showing a best-fit slope age of 75 kyr. After McDougall et al. (1969).

Fig. 10.6. Schematic K–Ar isochron diagram to show the effect of mixing inherited and radiogenic argon (A, B and C), coupled with variable atmospheric contamination (D, E and F). After Roddick and Farrar (1971).
FIGURE 6.3 Whole rock K–Ar isochron of Tuff IB from Olduvai Gorge, Tanzania. Data from Fitch et al. (1976) and Curtis and Hay (1972).

Figure 7-3 Generalized stratigraphy of the Koobi Fora Formation to the east of Lake Turkana, showing the main tuffaceous horizons. Average K/Ar ages and 40Ar/39Ar ages derived from step heating experiments, measured on feldspars from pumices, are shown: the number of samples used in calculating each mean is given in parentheses after each age. The right-hand column lists mean 40Ar/39Ar ages from multiple single-crystal measurements (number of crystals in parentheses) on feldspars from pumices. All uncertainties given are standard deviations of the respective populations. Note that some data from Kanapoi also are shown (after Leakey et al., 1995, 1998). Information mainly from Brown and Feibel (1986, 1991) and McDougall (1985, 1995, unpublished).
Figure 4. Ages of volcanoes in Hawaiian Emperor chain as function of distance from Kilauea Volcano on Hawaii. Error bars indicate standard deviations, queried where unknown. Where not shown, estimated errors are included within diameter of point. Dashed lines are for reference only and have no interpretive significance. Data for principal Hawaiian Islands from McDougall (1964), McDougall and Swanson (1972), Doollel and Dalrymple (1973), and Jackson and others (1972); for Nihoa, Necker, French Frigate, and Midway from Dalrymple and others (1974); for Koko from Clague and Dalrymple (1973) and Bukry (1974, written commun.); for Suiko from Ozima and others (1970); for Meiji from Worsley (1973); for Kanmu from Sachs (1972, written commun., quoted in Clague and Jarrard, 1973).

Figure 6.5 Average K–Ar date of the shield-building stage of volcanic activity of the Hawaiian Islands and distance from the volcano Kilauea on Hawaii (Figure 6.4). Data from McDougall and Duncan (1980).
Fig. 10.7. Plot of apparent K–Ar mineral ages against outward distance from the contact of the 60-Myr-old Eldora stock, Colorado. After Hart (1964).

Fig. 6.2 The K–Ar dates of minerals in the Snowbank stock (2.6 Ga) as a function of distance from the intrusive contact of the Duluth Gabbro (1.05 Ga) in Minnesota. Data from Hanson and Gast (1967).
FIGURE 6.12 Contour map of K–Ar dates of biotites in the Idaho batholith on northwestern Montana and Idaho based primarily on the data of Criss et al. (1982). The areas in black are Eocene plutons that intruded the Cretaceous rocks of the batholith and caused partial losses of $^{40}$Ar from biotite in the contact zone. The profile of K–Ar dates was drawn along the line A–B. Adapted from Criss et al. (1982).

FIGURE 6.14 Retention of $^{40}$Ar by minerals as a function of depth in the continental crust. The blocking temperatures are 230°C (K-feldspar), 373°C (biotite), and 685°C (hornblende). The geothermal gradient is 23°C/km, the average surface temperature is 15°C, and the relation between depth and the geothermal temperature is assumed to be linear. The resulting depth for zero K–Ar dates are 9.3 km (K-feldspar), 15.5 km (biotite), and 29.1 km (hornblende). The Mohorovicic Discontinuity was placed at a depth of 45 km. Blocking temperatures from Berger and York (1981).
\[ ^{40}\text{Ar}/^{39}\text{Ar} \]

main advantages:
1. measurement of P and D in same aliquot
2. get domain/zonation information

\[ ^{39}\text{K}(n,p)^{39}\text{Ar} \]

or

\[ ^{39}\text{K} + ^{1}\text{n} \rightarrow ^{39}\text{Ar} + ^{1}\text{H} \]

neutrons have to be "fast"...(high E, >\~0.1 MeV)
Figure 2-2 Schematic diagrams showing model $^{40}$Ar/$^{39}$Ar age spectra. The top diagram portrays an idealized crystal in cross section, the middle diagram in each panel shows the concentration of radiogenic argon and neutron-induced $^{39}$Ar$_K$ across the crystal, and the lower diagram illustrates the $^{40}$Ar/$^{39}$Ar age spectrum expected from measurement of argon extracted in successive steps at progressively higher temperature from the idealized crystal. (a) The case of a crystal undisturbed subsequent to initial crystallization and rapid cooling. (b) The case in which partial loss of radiogenic argon has occurred from the crystal in geologically recent times, so that there is a marked gradient of radiogenic argon across the crystal from essentially zero at the grain boundary. (c) The same case as in (b), except that significant accumulation of radiogenic argon has occurred since the reheating event owing to the passage of time. A maximum age for the time of the reheating is given by the $^{40}$Ar/$^{39}$Ar age for the gas released in the first step of the experiment, and a minimum age for the primary crystallization of the crystal is provided by the apparent age measured on the gas released at the highest temperature. Thickness of bars in model age spectra indicates nominal uncertainty in the individual ages.
Φ(ε) = flux density of neutrons of energy ε  \([=]\) (nV)/(cm\(^2\)s)  
σ(ε) = capture cross-section of neutrons of energy ε  \([=]\) barns  
Δt = duration of irradiation
where $t_s$ is age of standard

so, for an unknown...

$$t = \frac{1}{\lambda} \ln \left[ 1 + J \frac{40\text{Ar}^*}{39\text{Ar}_K} \right]$$
Fig. 9.5. Two schemes for irradiating samples and standards. Scheme A allows detection only of vertical neutron fluence gradients and its use is declining as demands for precise knowledge of $J$-values increases. Scheme B allows tight control of horizontal neutron fluence by close bracketing or interpolation of $J$-values.

Fig. 9.6. Typical neutron fluence gradients corresponding to sample irradiation geometries shown in Fig. 9.5. (a) Vertical fluence gradient for an irradiation in the US Geological Survey TRIGA reactor. (Source: adapted from Dalymple et al. [1981].) (b) Lateral fluence gradient for an irradiation in the Oregon State University TRIGA reactor. (Source: Renne et al. [2015]. Reproduced with permission of The American Association for the Advancement of Science.) Both panels show the parameter $J$ normalized to its maximum value.
\[ ^{40}\text{K} (n,p) \rightarrow ^{40}\text{Ar} \]
\[ ^{40}\text{Ca} (n,n\alpha) \rightarrow ^{36}\text{Ar} \]
\[ ^{42}\text{Ca} (n,\alpha) \rightarrow ^{39}\text{Ar} \]

can minimize to some degree by positioning in reactor...
...but in reality need to make corrections.

Fig. 10.8. Part of the chart of the nuclides in the region of potassium, showing the production reaction (heavy arrow) and major interfering reactions (solid) during neutron activation. The dashed reaction to \(^{37}\text{Ar}\) is the interference monitor. Data from Mitchell (1968).
$^{40}\text{K} (n,p)^{40}\text{Ar}$

irradiate a sample with high K and no Ar (e.g., $\text{K}_2\text{SO}_4$ or K-doped glass), then measure $^{40}\text{Ar}$ in it. Then correction

$$
(\frac{^{40}\text{Ar}}{^{39}\text{Ar}})_K = (\frac{^{40}\text{Ar}}{^{39}\text{Ar}})_m - (\frac{^{36}\text{Ar}}{^{39}\text{Ar}})_m \times (\frac{^{40}\text{Ar}}{^{36}\text{Ar}})_{\text{air}}
$$

or

$$
(\frac{^{40}\text{Ar}}{^{39}\text{Ar}})_K = (\frac{^{40}\text{Ar}}{^{39}\text{Ar}})_m - (\frac{^{36}\text{Ar}}{^{39}\text{Ar}})_m \times 298.6
$$

as measured in the K-doped glass
\[ ^{40}\text{Ca} (n, n\alpha)^{36}\text{Ar} \]

- especially important for samples with high Ca/K, like hornblende, plagioclase
- critical because \(^{36}\text{Ar}\) is used for atmospheric contamination
- related reaction also makes \(^{37}\text{Ar}\)

\[ ^{40}\text{Ca} (n, n\alpha)^{36}\text{Ar} \quad ^{40}\text{Ca} (n, \alpha)^{37}\text{Ar} \]

So, just irradiate \(\text{CaF}_2\), and measure

\[
\left(\frac{^{36}\text{Ar}}{^{37}\text{Ar}}\right)_{\text{Ca}} = \left(\frac{^{36}\text{Ar}}{^{37}\text{Ar}}\right)_m - \left(\frac{^{40}\text{Ar}}{^{37}\text{Ar}}\right)_m \left(\frac{^{36}\text{Ar}}{^{40}\text{Ar}}\right)_{\text{air}}
\]

or

\[
\left(\frac{^{36}\text{Ar}}{^{37}\text{Ar}}\right)_{\text{Ca}} = \left(\frac{^{36}\text{Ar}}{^{37}\text{Ar}}\right)_m - \left(\frac{^{40}\text{Ar}}{^{37}\text{Ar}}\right)_m \times \frac{1}{298.6}
\]

as measured in the \(\text{CaF}_2\)

but be careful, because \(^{37}\text{Ar}\) has \(t_{1/2} \sim 35\) days!
$^{42}\text{Ca} \ (n, \alpha) \ ^{39}\text{Ar}$

in Ca salt, both $^{39}\text{Ar}$ and $^{37}\text{Ar}$ are produced from Ca, so $(^{39}\text{Ar} / ^{37}\text{Ar})_{\text{Ca}}$ is a direct measurement on the Ca-salt
\[ \frac{^{40}\text{Ar}^*/^{39}\text{Ar}_K}{^{40}\text{Ar}/^{39}\text{Ar}}_m = \frac{^{40}\text{Ar}/^{39}\text{Ar}}_m - 298(^{36}\text{Ar}/^{39}\text{Ar})_m + 298(^{36}\text{Ar}/^{37}\text{Ar})_\text{Ca}(^{37}\text{Ar}/^{39}\text{Ar})_m - \left[ \frac{^{40}\text{Ar}/^{39}\text{Ar}}_K \right] \]

- atmospheric correction
- \(^{36}\text{Ar}\) from \(^{40}\text{Ca}\) during irradiation
- \(^{39}\text{Ar}\) from \(^{42}\text{Ca}\) during irradiation
- \(^{40}\text{Ar}\) from \(^{40}\text{K}\) during irradiation

also
- need to adjust all values for mass discrimination effects
- need to recognize that extraterrestrial samples have different atmospheric compositions (and cosmogenic ones)
other reactions to worry about

1) $^{35}\text{Cl} (n,\gamma) ^{36}\text{Cl} \rightarrow ^{36}\text{Ar} \quad t_{1/2} = 300,000 \text{ a}

2) $^{37}\text{Cl} (n,\gamma) ^{38}\text{Cl} \rightarrow ^{38}\text{Ar} \quad t_{1/2} = 37.3 \text{ min}

1) If you have high Cl/Ar samples (e.g., hornblende) and wait ~ a year before analyzing them, this can be a few percent problem

2) Will mostly have decayed by time of analysis, so
   a) can get Cl content of sample (or step) from $^{38}\text{Ar}$... (often correlated with excess $^{40}\text{Ar}$)
   b) can correct for $^{36}\text{Ar}$ from $^{36}\text{Cl}$ (from $^{35}\text{Cl}$)
Figure 3-12 Schematic diagram of an argon extraction system in use in the Research School of Earth Sciences (RSES) in the Australian National University (ANU). Note that the system is directly on-line to the mass spectrometer and that extraction of argon from samples can be done either in the resistance furnace or in the laser cell, under computer control. Most valves are operated pneumatically under computer control, so that the extraction of argon and subsequent isotopic analysis is carried out through prewritten programs. Not to scale. Modified from diagram prepared by G.E. Batt.
Figure 3-23 Plot of apparent age, determined using UV laser microprobe transects, versus distance across a metamorphic biotite grain from a pegmatite within the Sesia Zone, Italian Alps, after Pickles et al. (1997), with permission of the authors and Elsevier Science.

McDougall & Harrison, 1999

Kelley and Wartho, 2000
1) Simple, closed-system behavior

Figure 4-1 (a) Simple case in which the concentrations of $^{40}$Ar and $^{39}$Ar are uniform across a solid following neutron irradiation. The concentration of $^{40}$Ar is twice that of $^{39}$Ar. (b) Age spectrum for the case shown in (a) assuming that the uniformly distributed $^{40}$Ar and $^{39}$Ar were both transported to the surface by volume diffusion and then released from the solid.

Figure 4-2 The age spectrum for sanidine sample 92-176 from the Fish Canyon Tuff, Colorado. The uniform values of $^{40}$Ar/$^{39}$Ar throughout the step-heating experiment are taken as evidence that the radiogenic argon is distributed uniformly within the crystals. After Spell and McDougall (unpublished), using GA1550 biotite, with reference age of 98.8 Ma, as fluence monitor.

Figure 4-3 Age spectrum for GA1550 biotite from the Mount Dromedary complex, New South Wales, Australia. After Tetley (1978). This spectrum conforms well with that expected from a sample that has remained thermally undisturbed since crystallization and rapid cooling.

plateaux: no single definition, but typically >4-5 steps that agree within 95% confidence and represent >50% of gas released
1) Conventional isochron
dispersion of points along line is due to not just different P/D, but also mixing with
trapped component and radiogenic Ar
drawbacks to conventional isochron:
1) $^{36}\text{Ar}$ is measured with lowest precision (only 0.337% of Ar, typically)
2) "open-ended" (steps with lots of radiogenic $^{40}\text{Ar}$ plot way out and dominate regression, precluding precise determination of trapped component
Inverse isochron

\[
\frac{^{40}\text{Ar}^*}{^{39}\text{Ar}} = \frac{1}{J} (e^{t} - 1)
\]

Deviations from line can result from \(^{40}\text{Ar}^*\) loss (e.g., slow cooling or reheating) and/or multiple trapped components.
2. Excess Ar and the Trapped Component

Figure 4-9 Isochron plot for biotite sample H7f (fig. 4-8) yields a well correlated array that appears to reflect the presence of two argon components; uniformly distributed $^{40}\text{Ar}^*$ produced in situ and a trapped component with a $^{40}\text{Ar} / ^{36}\text{Ar}$ of 375 ± 15.

Trapped component has higher $^{40}\text{Ar} / ^{36}\text{Ar}$ than atmosphere

Figure 4-8 Age spectrum of biotite sample H7f from the study of Heizler and Harrison (1988) yields a spectrum that is characterized by high initial ages that decrease to a minimum value of about 13 Ma before rising again to a geologically implausible age. The form of this age spectrum is often associated with the presence of excess argon.

Non-ideal spectrum
2. Excess Ar and the Trapped Component

Being smart about the trapped component MAY allow you insight into complex step-heating spectra.
Pattern of step-heating spectrum can identify and mitigate excess $^{40}\text{Ar}$ (sometimes)

Figure 4-23 Age spectrum of a homogeneous hornblende that has taken up $^{40}\text{Ar}_\text{E}$. After Harrison and McDougall (1980b). Note the expanded scale on the inset. The $^{40}\text{Ar}_\text{E}$ is situated entirely at the grain margins.

Figure 4-24 Age spectra of calcic plagioclases from amphibolites, Broken Hill, Australia. After Harrison and McDougall (1981). The saddle-shaped release patterns are characteristic of $^{40}\text{Ar}_\text{E}$ and may result from the contaminating argon being held in two different lattice sites with contrasting thermal degassing behavior. Note that the $^{40}\text{Ar}_\text{E}$ is released both in the initial and final stages of gas release.
Excess $^{40}\text{Ar}$ and anomalous Cl are often correlated.

1) $^{35}\text{Cl (n,}\gamma^{)}^{36}\text{Cl} \rightarrow ^{36}\text{Ar}$ \hspace{1cm} t$_{1/2} = 300,000$ a
2) $^{37}\text{Cl (n,}\gamma^{)}^{38}\text{Cl} \rightarrow ^{38}\text{Ar}$ \hspace{1cm} t$_{1/2} = 37.3$ min

Figure 4-25 (a) Age spectrum of K-feldspar sample XH-9a showing profound differences in age between duplicate isothermal heating steps early in the gas release, from Harrison et al. (1994). The resulting plot of $\Delta^{(40}\text{Ar}^*/\text{K})$ versus $\Delta$(Cl/K) for this sample is shown in fig. 4-26(b).
3. Open-system complex behavior

Ar can move around in samples prior to analysis.

If this happens via thermally-activated volume diffusion, we can make sense of it.

Figure 4-13 The first age spectrum diagram. After Turner et al. (1966). Data from two separate irradiations of the Brudermheim chondrite are shown together with model age spectra for spheres of uniform radius and spheres with a lognormal distribution of radii that have undergone 90% radiogenic argon loss 0.5 Ga ago.

Figure 4-14 Theoretical age spectra for both aggregates of uniform spheres (solid lines) and a lognormal distribution of sphere radii (dashed lines). After Turner (1968), with permission of author and publisher. In this example, a 4.5-Ga-old sample has experienced varying degrees of radiogenic argon loss during an event 0.5 Ga ago.
The Ordovician L-chondrite event

most L-chondrites have high-T cooling ages of 465-500 Ma;
peak: 470 ± 6 Ma (Korochantseva et al., 2006)

small anomalously high peak in terrestrial craters 450-480 Ma
(Schmitz et al., 2001)
Ordovician L-chondrite event: The stratigraphic record

Fig. 1. The Mid-Ordovician Hälleklis section in southern Sweden. The red line represents the stratigraphic level (at –1 m in this study) that corresponds to the time of the breakup of the LCPB in the asteroid belt. At this level, there is a change in the strata in abundance and types of extraterrestrial chrome-spinel grains. A low-abundance, mixed micrometeorite assemblage is replaced by a high-abundance assemblage completely dominated by L-chondritic grains. At the same level, the grain size of bioclastic limestone fragments begins to increase, indicating onset of a gradual sea level fall that culminates with the conspicuous Täljsten lowstand deposit traceable over most of Baltoscandia and likely also globally. Asteroid breakup artwork by Don Davis. (Photo credit: Birger Schmitz, Lund University)

Schmitz et al. (2019)
Ordovician L-chondrite event: The fossil meteorite and ET spinel record

Schmitz et al. (2013; 2015)
Ordovician L-chondrite event: Cosmogenic $^{21}$Ne in fossil meteorites

Schmitz et al., 2015
Ordovician L-chondrite event: The fossil meteorite and ET spinel record

estimated flux increase ~10-200x

Schmitz et al., 2008