

# Diffusion in minerals and melts

There are three types of diffusion in a rock

- *Surface diffusion* – essentially over a 2 dimensional area
- *Grain-boundary diffusion* – along grain boundaries, slower than surface
- *Volume diffusion* – within a crystal or melt. Slowest

## Arrhenius equation:

- from observation, diffusivity increases with temperature
- from observation, a graph of  $\ln(D)$  vs.  $1/T$  gives a straight line
- the slope of the  $\ln(D)$  vs.  $1/T$  graph is related to the activation energy

# Arrhenius equation

$$D = D_0 \times e^{-E_a/RT} \rightarrow \ln D = \ln D_0 - E_a/RT$$

$$\mathbf{y = b + mx}$$

$D$  = diffusion coefficient,

$D_0$  = diffusion coefficient at infinite  $T$  (for  $T \rightarrow \infty$ )

$E_A$  = activation energy,

$R$  = gas constant in  $\text{J K}^{-1}\text{mol}^{-1}$ ,

$T$  = temperature in Kelvin

A graph of  $\ln D$  vs.  $1/T$  gives a straight line with a slope of  $-E_A/R$  and an intercept of  $\ln D_0$

Example: Diffusion is measured at four temperatures. What is the activation energy for the reaction?

T(°C)	$D$
747	$4.23 \cdot 10^{-16}$
791	$1.55 \cdot 10^{-15}$
838	$3.45 \cdot 10^{-15}$
890	$2.09 \cdot 10^{-14}$

$D$	T(K)	1/T	$\ln D$
4.23-16	1020	0.000980	-35.4
1.55-15	1064	0.000940	-34.1
3.45-15	1111	0.000900	-33.3
2.09-14	1163	0.000860	-31.5

D in cm<sup>2</sup>/sec

# Arrhenius equation

$$D = D_0 \times e^{-E_a/RT} \rightarrow \ln D = \ln D_0 - E_a/RT$$

$$\ln D = \ln D_0 - 1000 \cdot E_a / RT$$

Using  $y = mx + b$

$m = \text{slope and}$

Slope  $m = -E_a/R$

$-E = mR$

Slope  $m = -31148$

(from graph)

with  $R = 0.00831 \text{ kJ/K/mol}$

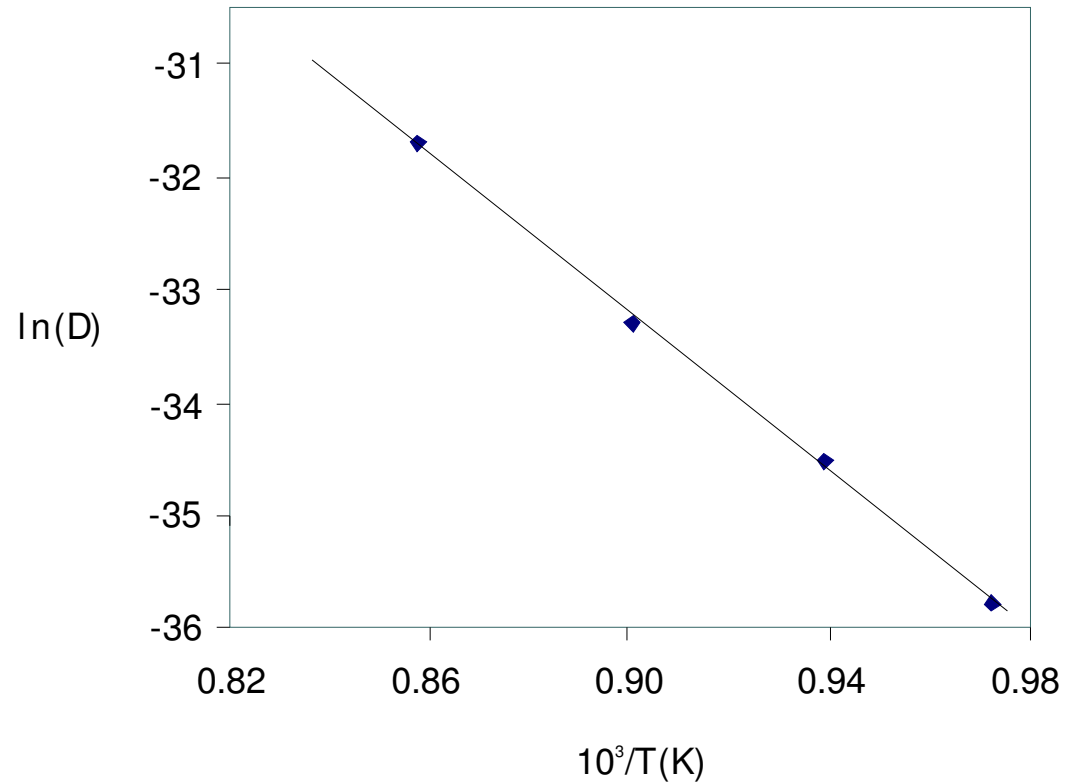
$-E_a = -31148 \times 8.31 \times 10^{-3}$

$D_0 = 0.061 \text{ cm}^2/\text{sec}$

Activation

energy:

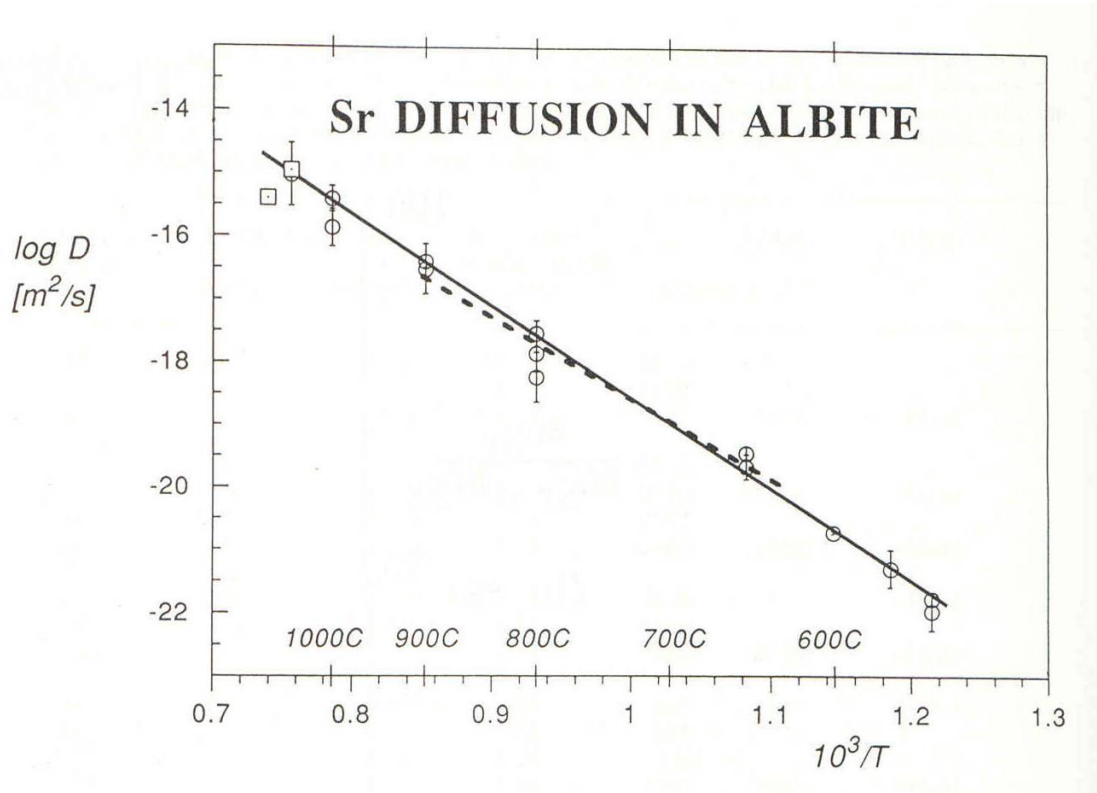
$E_a = 259 \text{ kJ/mol}$



# Diffusion in minerals and melts

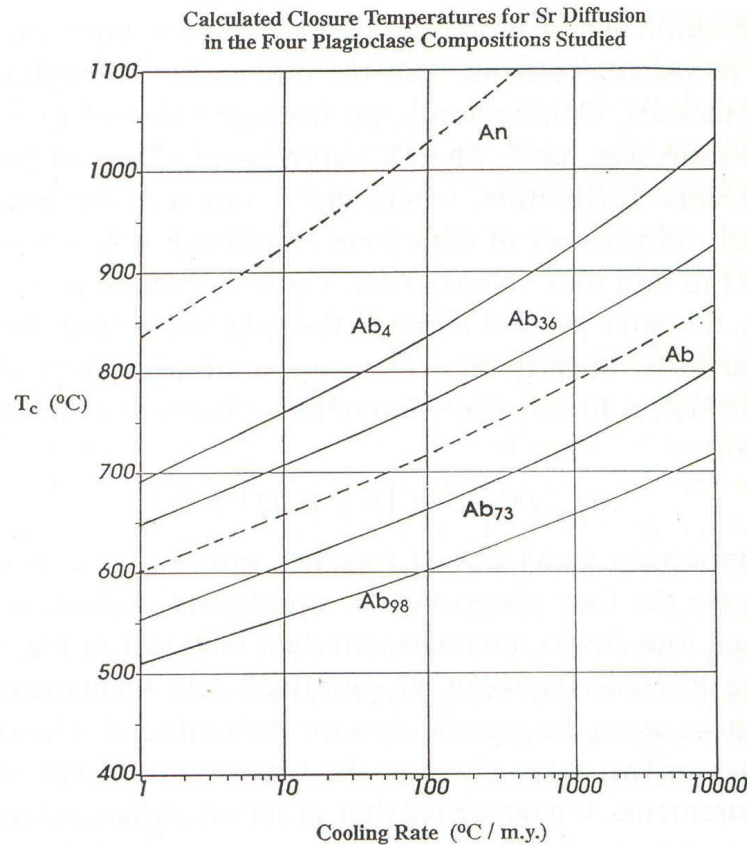
- Diffusivity is directly proportional to temperature.  
Weakly dependent on pressure
- Arrhenius equation is:  **$D = D_0 \exp(-E/RT)$**
- Where  $D_0$  is the diffusion coefficient at infinite T, E is the activation energy, R is the gas constant, and T is the temperature in Kelvin
- In crystals D ranges for magmatic temperatures from  $10^{-29}$  m<sup>2</sup>/s to  $10^{-8}$  m<sup>2</sup>/s.

# Diffusion in minerals and melts



Diffusion is thermally activated and obeys an Arrhenius law

# Diffusion in minerals and melts



Calculation of  
closure temperatures

$$T_c = \frac{E/R}{\ln \frac{ART_c^2(D_0/a^2)}{E dT/dt}} \quad \text{Dodson 1973}$$

E = activation energy

$D_0$  = Sr diffusion factor

R = gas constant

A = anisotropy factor

a = particle radius

dT/dt = cooling rate

The equation is solved by assuming a value  
For  $T_c$  and solving for  $T_c$  iteratively

# Closure Temperature

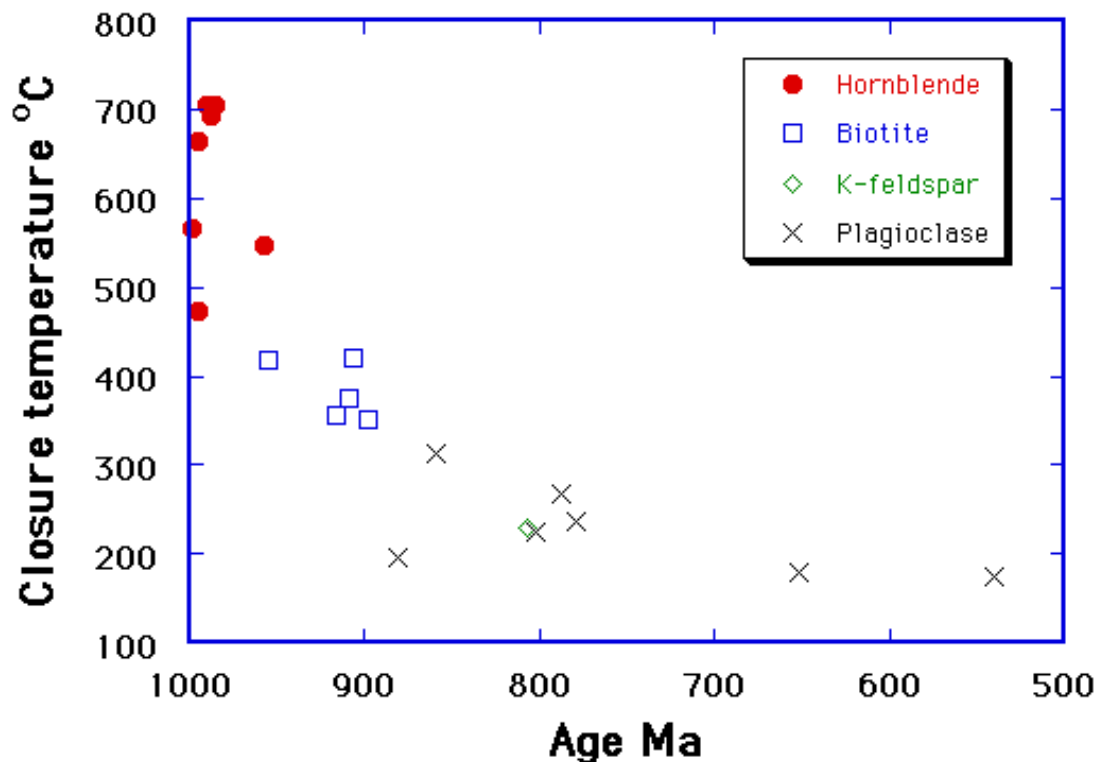
the temperature at which a cooling mineral can no longer exchange isotopes with its surroundings

<b>Mineral</b>	<b>Method</b>	<b>T (°C)</b>
Zircon	U-Pb	>800
Monazite	U-Pb	>800
Titanite (Sphene)	U-Pb	600
Garnet	Sm-Nd	>550
Hornblende	K-Ar	500
Muscovite	Rb-Sr	500
Muscovite	K-Ar	350
Apatite	U-Pb	350
Biotite	Rb-Sr	300
Biotite	K-Ar	280
K-Feldspar	K-Ar	200
Apatite	Fission Track	120

Closure temperatures for common minerals for different isotopic systems. Note that closure temperatures for different systems in the same minerals can vary.

# K-Ar Method

## Closure temperature and cooling ages



- Different minerals become "closed" to Ar diffusion at different temperatures.
- Ar continues to diffuse out of plagioclase until it has cooled below about 300°C, whereas hornblende becomes closed to Ar diffusion at about 600°C.

# K-Ar Method

Potassium (K) naturally occurs in 3 isotopes:

$^{39}\text{K}$  (93.2581 %)

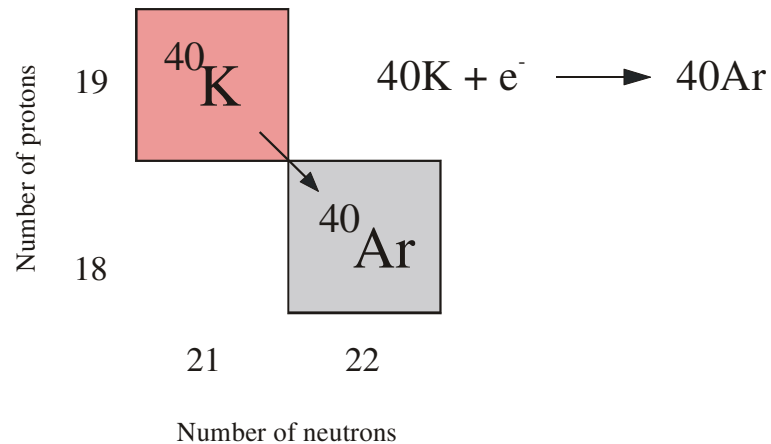
$^{40}\text{K}$  (0.0117 %)

$^{41}\text{K}$  (6.7302 %)

$^{36}\text{Ar}$  (0.337 %)

$^{38}\text{Ar}$  (0.063 %)

$^{40}\text{Ar}$  (99.60 %)



$^{40}\text{K}$  is a radioactive isotope of potassium

- Half-life 1.28 Ga
- $^{40}\text{K}$  (the radioactive isotope converts to Ca and Ar)
- Measure the ratio of Argon to Potassium
  - Provides age

# K-Ar Method

## Literature

Dalrymple, G. B. and Lanphere, M. A. (1969)  
*Potassium - Argon Dating*. Freeman, 258 pp.

McDougall, I. and Harrison, T. M. (1999)  
*Geochronology and Thermochronology by the  $^{40}\text{Ar}/^{39}\text{Ar}$  Method*, 2nd Edn. Oxford Univ. Press, 269 pp.

<http://www.onafarawayday.com/Radiogenic/Ch10/Ch10-1.htm>

# K-Ar method

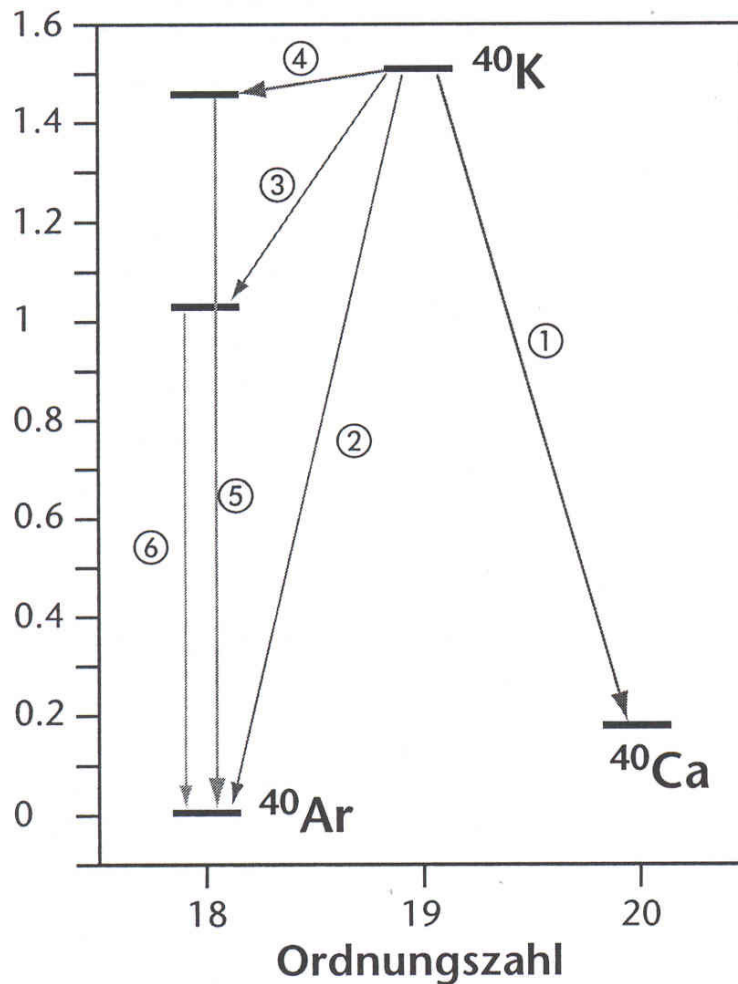
- General Principles
  - used in igneous rocks and minerals
    - Basalt
    - Tephra (Volcanic Ash)
    - Pumice
    - Mica (biotite, muscovite), amphibol, K-feldspar
  - age
    - more Ar-the older the rock/mineral
    - less Ar-the younger the rock/mineral

# K-Ar method

- K is very common in the crust of the Earth so method can be applied widely
- One must correct for the fact that only 11.2% of the  $^{40}\text{K}$  decays to  $^{40}\text{Ar}^*$  by electron capture (88.8% of  $^{40}\text{K}$  decays via  $\beta^-$ -decay to  $^{40}\text{Ca}$ )
- Ages obtained by this method may not agree with other methods due to Ar loss

# K-Ar Methode

Zerfallsschema von  $^{40}\text{K}$



- ① 88.8% machen einen  $\beta^-$ -Zerfall in den Grundzustand von  $^{40}\text{Ca}$  (Zerfallsenergie 1.32 MeV)
- ② 0.16% machen einen Elektroneneinfang in den Grundzustand von  $^{40}\text{Ar}$  (Zerfallsenergie 1.51 MeV)
- ③ 0.001% machen einen  $\beta^+$ -Zerfall in einen angeregten Zustand von  $^{40}\text{Ar}$  (Zerfallsenergie 0.49 MeV)
- ④ 11.0% machen einen Elektroneneinfang in einen angeregten Zustand  $^{40}\text{Ar}$  (Zerfallsenergie 0.05 MeV)
- ⑤ ⑥ Zerfall der angeregten Zustände von  $^{40}\text{Ar}$  in den Grundzustand unter  $\gamma$ -Emission

# K-Ar Method

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

$$\lambda = \lambda_e + \lambda_\beta$$

$$\lambda_e = 0.581 \times 10^{-10} \text{y}^{-1}$$

$$\lambda_\beta = 4.962 \times 10^{-10} \text{y}^{-1}$$

$$\lambda = (0.581 + 4.962) \times 10^{-10} = 5.543 \times 10^{-10} \text{y}^{-1}$$

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

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where:  ${}^{40}\text{Ar}^*$  = the number of 40 Argon atoms after time t

${}^{40}\text{K}$  = the number of 40 Potassium atoms

$\lambda_e$  = decay constant of  ${}^{40}\text{K}$  to  ${}^{40}\text{Ar}$

$\lambda$  = total decay constant of  ${}^{40}\text{K}$

t = time

e = logarithm to the base e

# K-Ar Method

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

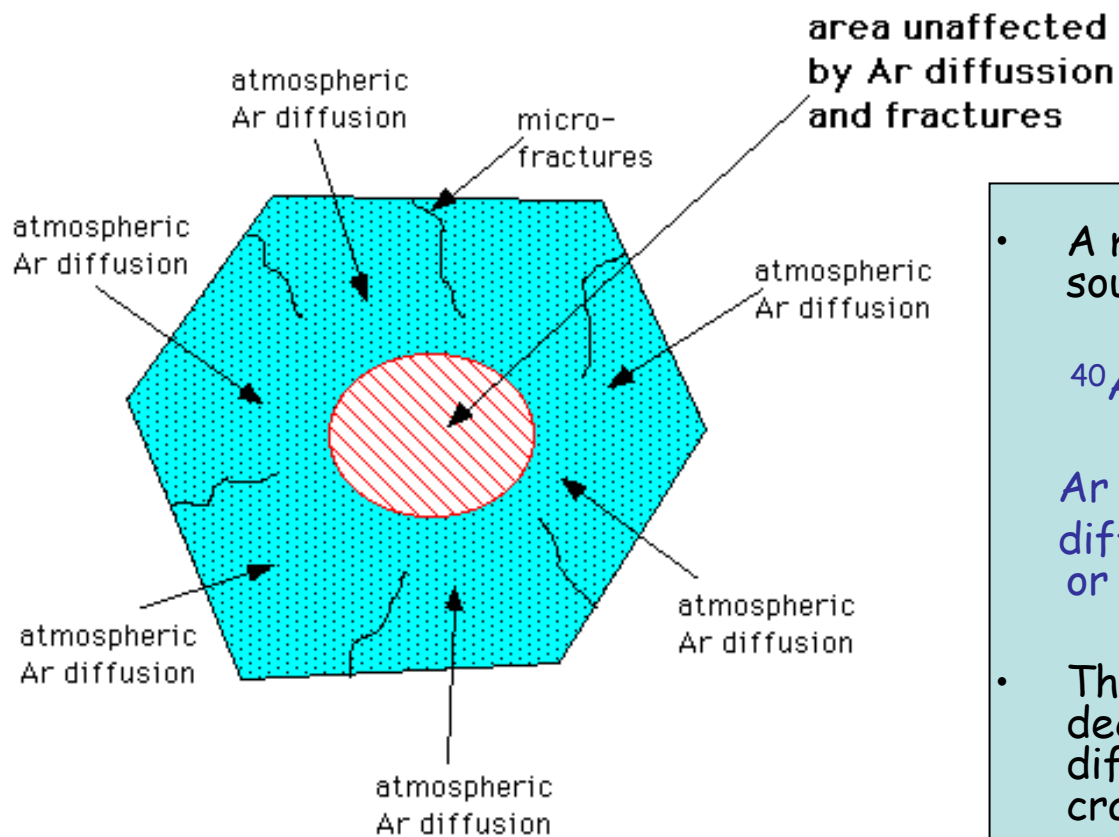
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where:  $t$  = age  
 $\lambda$  = total decay constant of  ${}^{40}\text{K}$   
 $\lambda_e$  = decay constant of  ${}^{40}\text{K}$  to  ${}^{40}\text{Ar}$   
 ${}^{40}\text{Ar}^*$  =  ${}^{40}\text{Ar}$  produced by *in situ* decay of  ${}^{40}\text{K}$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

# K-Ar method

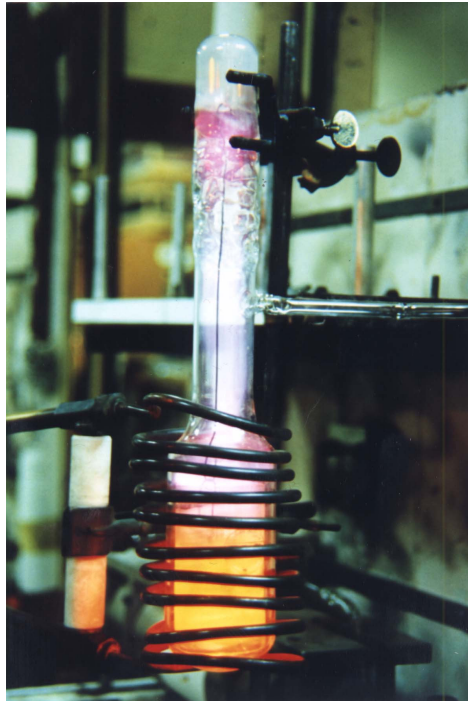
- Mineral forms and cools
  - Mineral at time of formation has K but no Ar
  - After mineral has formed or cooled to certain temperature ( $\rightarrow$  closure temperature) its radiometric clock starts and  $^{40}\text{Ar}^*$  is accumulated through decay of  $^{40}\text{K}$

# K-Ar method

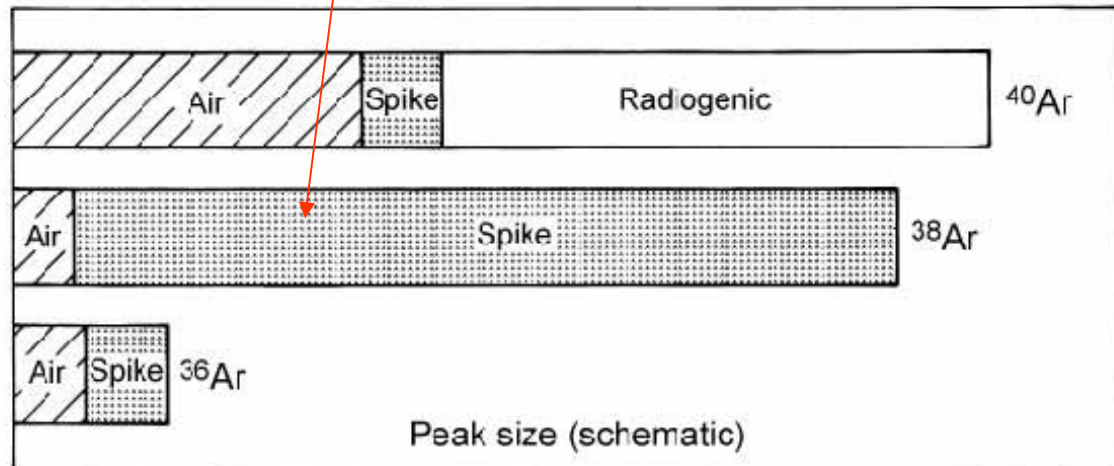
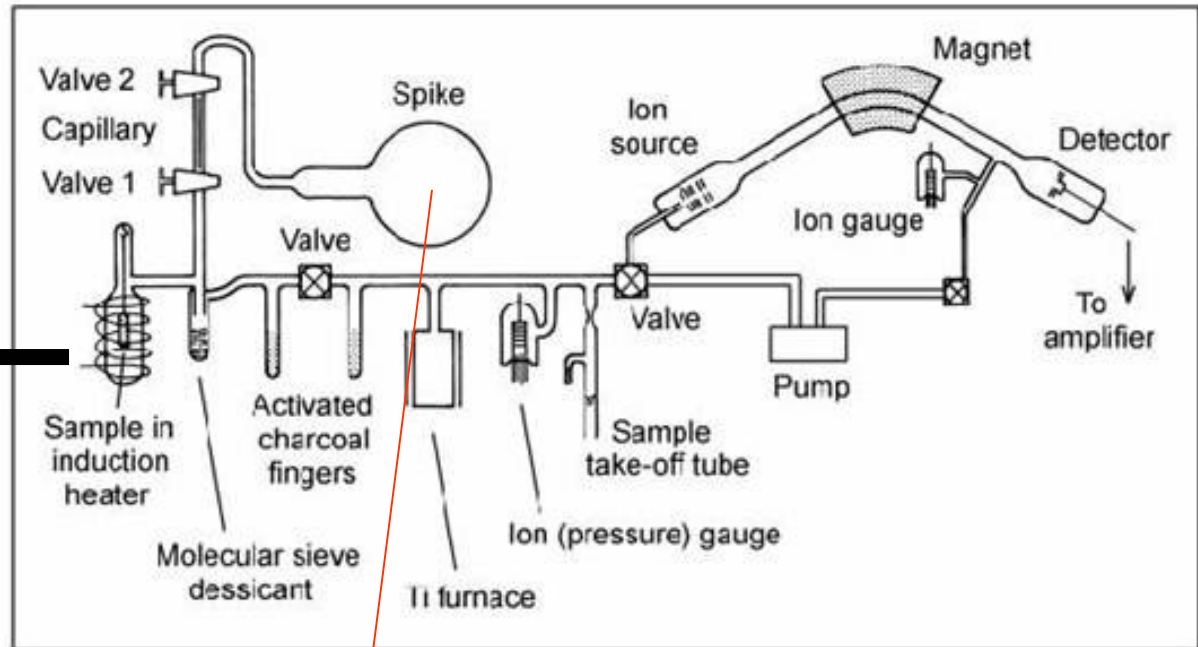


- A mineral can contain a number of sources of Ar:
  - $^{40}\text{Ar}$  derived from the decay of  $^{40}\text{K}$
  - Ar that enters the crystal by diffusion through the crystal lattice or along microfractures
- The radiogenic Ar released from the decay of  $^{40}\text{K}$  in the mineral can also diffuse out of the grain along the cracks.

# K-Ar method



Resistance furnace



# K-Ar Method

Example: K = 8.378%,  $^{40}\text{Ar}^*$  = 0.3305 ppm

Calculate  $^{40}\text{Ar}^*/^{40}\text{K}$  ratio

$$= \frac{0.3305 \times 39.098304 \times A}{8.378 \times 10^4 \times 0.0001167 \times 39.9623 \times A} = 0.03307$$

A = Avogadro's number =  $6.02 \times 10^{23}$

39.098304 = atomic weight of potassium

39.9623 = atomic weight of  $^{40}\text{Ar}$

$$T = \frac{1}{5.543 \times 10^{-10}} \ln \left[ \frac{0.03307 \times 5.543}{0.581} + 1 \right]$$

T = 494.7 Ma (mega anna)

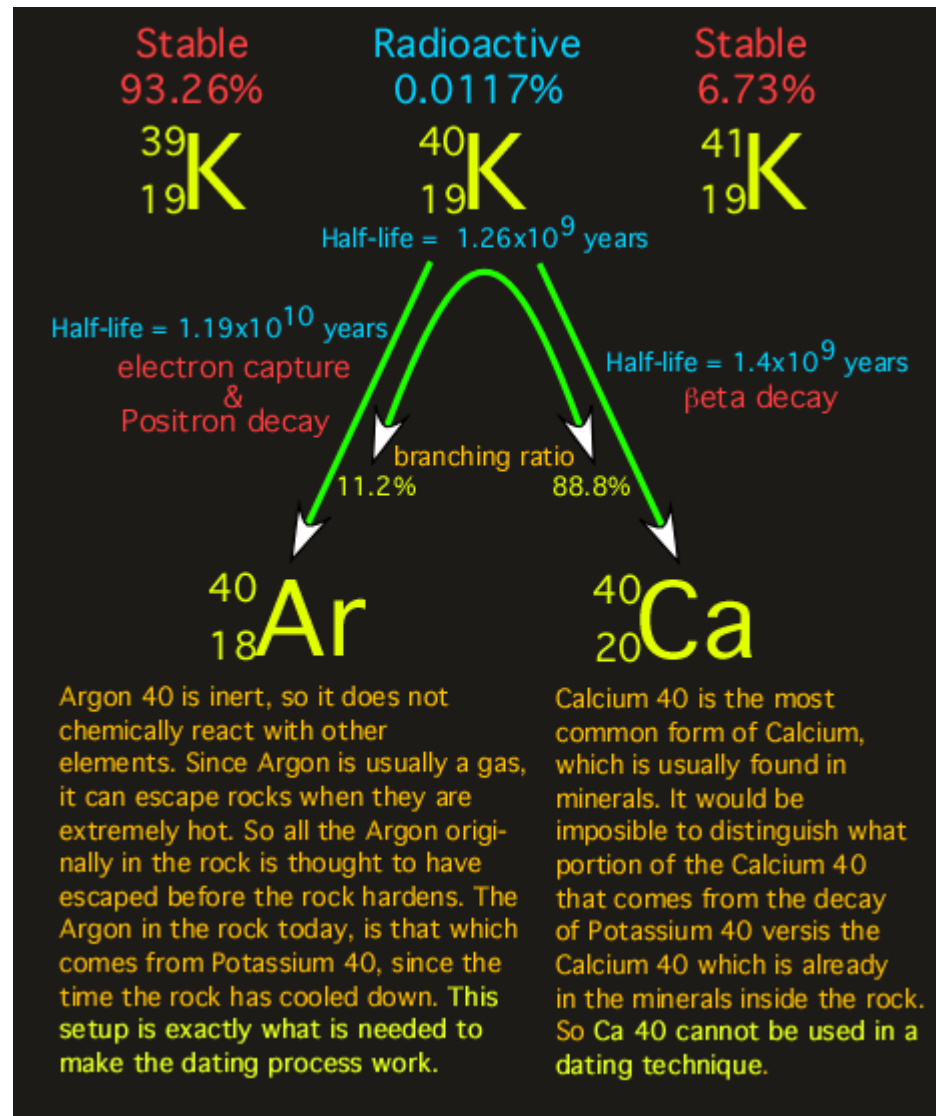
# K-Ar Method

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

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

# K-Ca Methode



# $^{40}\text{Ar}$ - $^{39}\text{Ar}$ dating

## Principles

Developed by Merrihue and Turner

Merrihue, C. and Turner, G. (1966). Potassium-argon dating by activation with fast neutrons. J. Geophys. Res. **71**, 2852-7

Method demands no addition of spike

No K determination

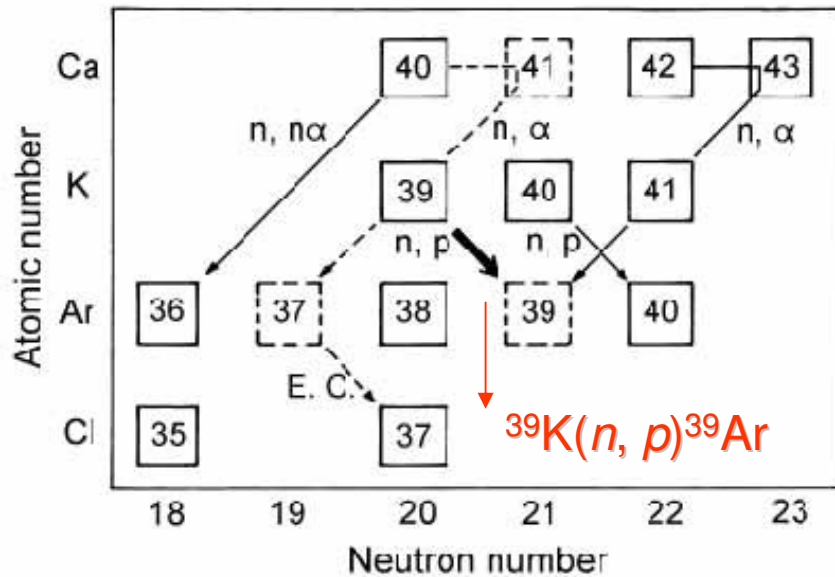
Only measurements of the Ar isotope ratios

Dating of small samples; also: in situ laser dating

**Irradiation of K-bearing sample in nuclear reactor**

# $^{40}\text{Ar}$ - $^{39}\text{Ar}$ dating

## Irradiation corrections



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

Beneficial reactions
  Undesirable reactions  
 Insignificant reactions

Production reaction (heavy arrow) and major interfering reactions (solid) during neutron activation. Dashed reaction to  $^{37}\text{Ar}$  is the interference monitor (Mitchell 1968)

$^{39}\text{Ar}$  is unstable with half life of 269 years

# $^{40}\text{Ar}$ - $^{39}\text{Ar}$ dating

Number of  $^{39}\text{Ar}$  atoms formed in the sample in the reactor:

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

$$^{39}\text{Ar} = ^{39}\text{K} \Delta T \int \varphi(\varepsilon) \sigma(\varepsilon) d\varepsilon$$

$$\frac{^{40}\text{Ar}^*}{^{39}\text{Ar}} = \frac{\lambda_e}{\lambda} \frac{^{40}\text{K}}{^{39}\text{K}} \frac{1}{\Delta T} \frac{e^{\lambda t} - 1}{\int \varphi(\varepsilon) \sigma(\varepsilon) d\varepsilon}$$

$\Delta T$  = length of irradiation

$\varphi(\varepsilon)$  = neutron flux density

$\sigma(\varepsilon)$  = capture cross section

$\varepsilon$  = energy

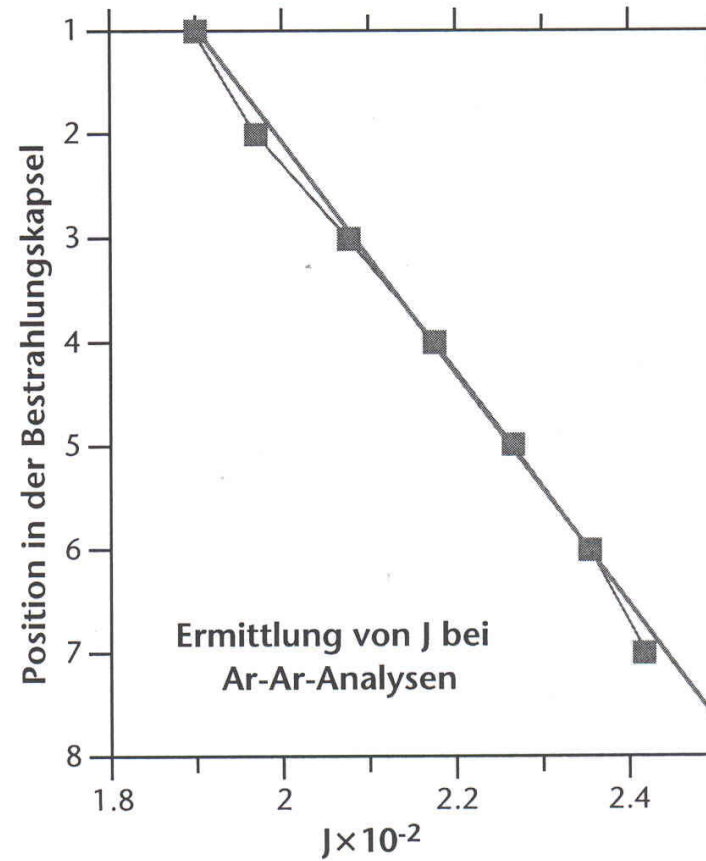
$$\frac{^{40}\text{Ar}^*}{^{39}\text{Ar}} = \frac{e^{\lambda t} - 1}{J}$$

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

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

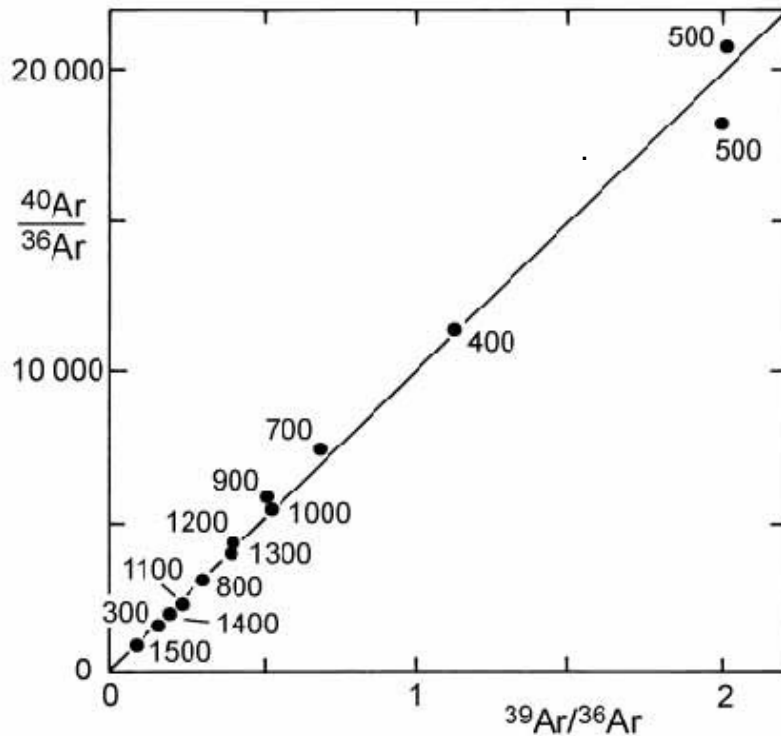
# $^{40}\text{Ar}$ - $^{39}\text{Ar}$ dating

Flux monitor

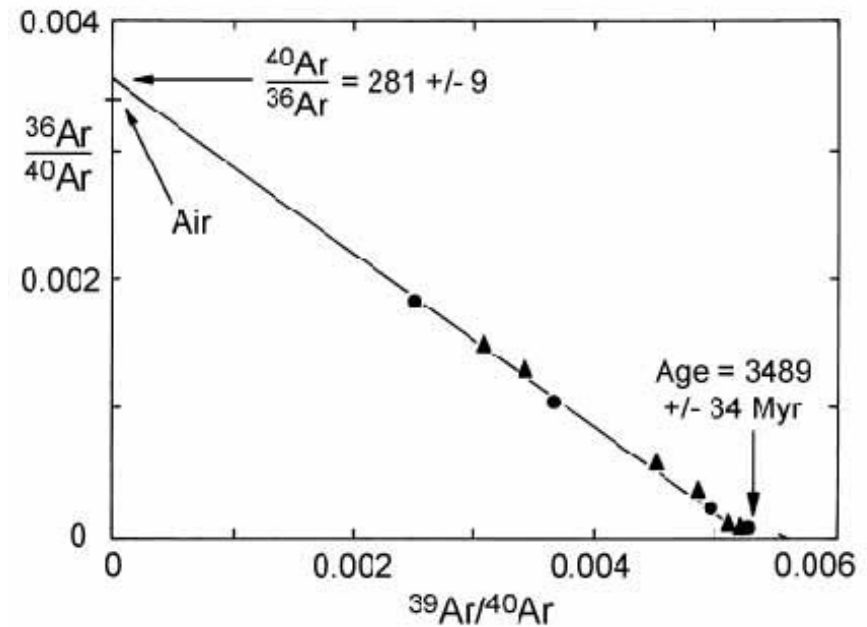


# $^{40}\text{Ar}$ - $^{39}\text{Ar}$ dating

## Data presentation



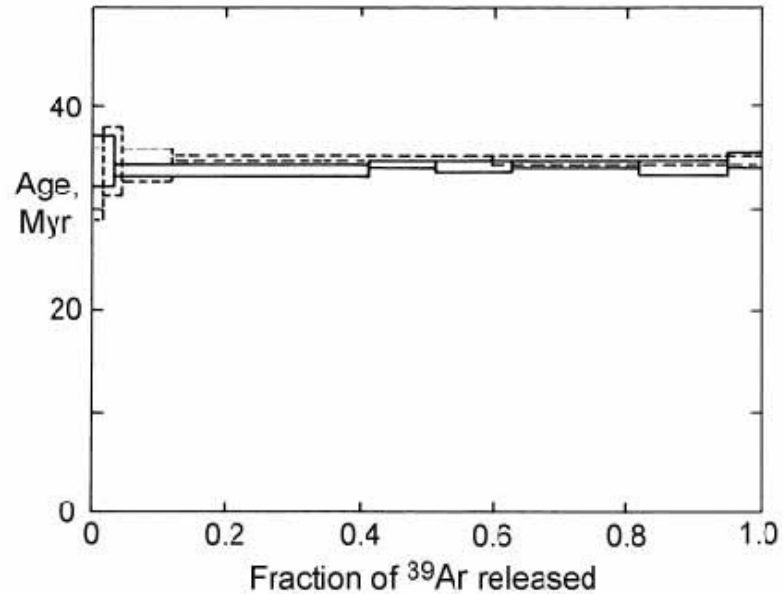
Step heating data for the Bjurbole meteorite presented on the Ar-Ar isochron diagram. Numbers by data points signify temperatures of each release step in  $^{\circ}\text{C}$ . After Merrihue and Turner (1966).



Inverse Ar-Ar isochron plot for the Barberton komatiite. The age is determined from the intersection on the x axis. After Lopez Martinez *et al.* (1984).

# $^{40}\text{Ar}$ - $^{39}\text{Ar}$ dating

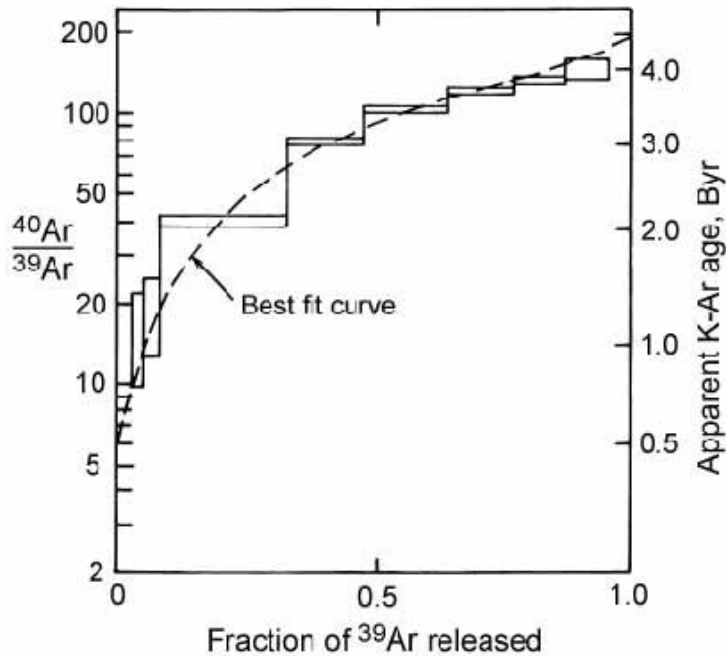
## Data presentation



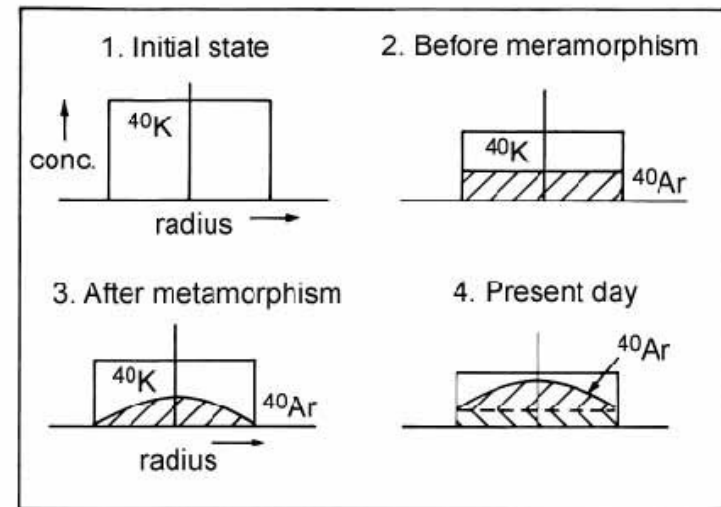
Ideal  $^{40}\text{Ar}/^{39}\text{Ar}$  age spectra for two tektite glasses, distinguished by solid and dashed boxes. After York (1984).

# $^{40}\text{Ar}$ - $^{39}\text{Ar}$ dating

## Argon loss events



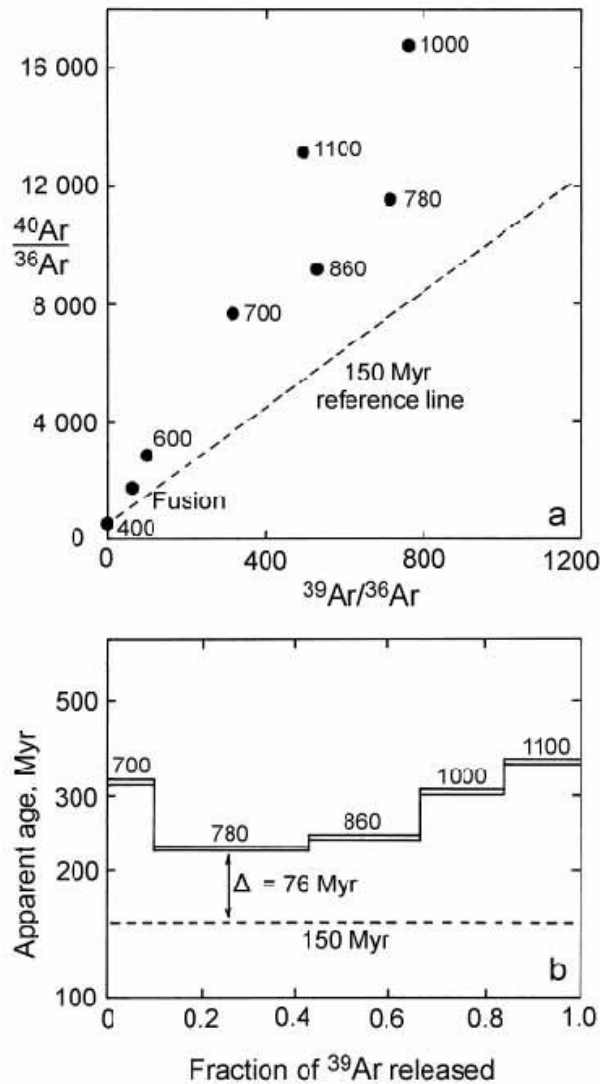
$^{40}\text{Ar}/^{39}\text{Ar}$  argon release pattern for the Colby chondritic meteorite (WR), showing evidence for disturbance after formation. The best fit curve is consistent with a model in which 40% of argon was lost during a thermal event at 500 Ma (collision between planetesimals?). Turner (1968).



Schematic illustration of the geological history of a mineral grain in a partially disturbed meteorite. 1) at 4500 Myr; 2) 500 Myr ago, before thermal event; 3) immediately after the event; 4) present day. Turner (1968).

# $^{40}\text{Ar}$ - $^{39}\text{Ar}$ dating

## Excess (inherited) argon



Comparison between the isochron plot (above) and age spectrum plot (below) for a biotite grain from kimberlite with **excess argon**.

Note the characteristic 'saddle shaped' profile. Numbers indicate the temperature of each heating step in  $^{\circ}\text{C}$ . After Lanphere and Dalrymple (1976).

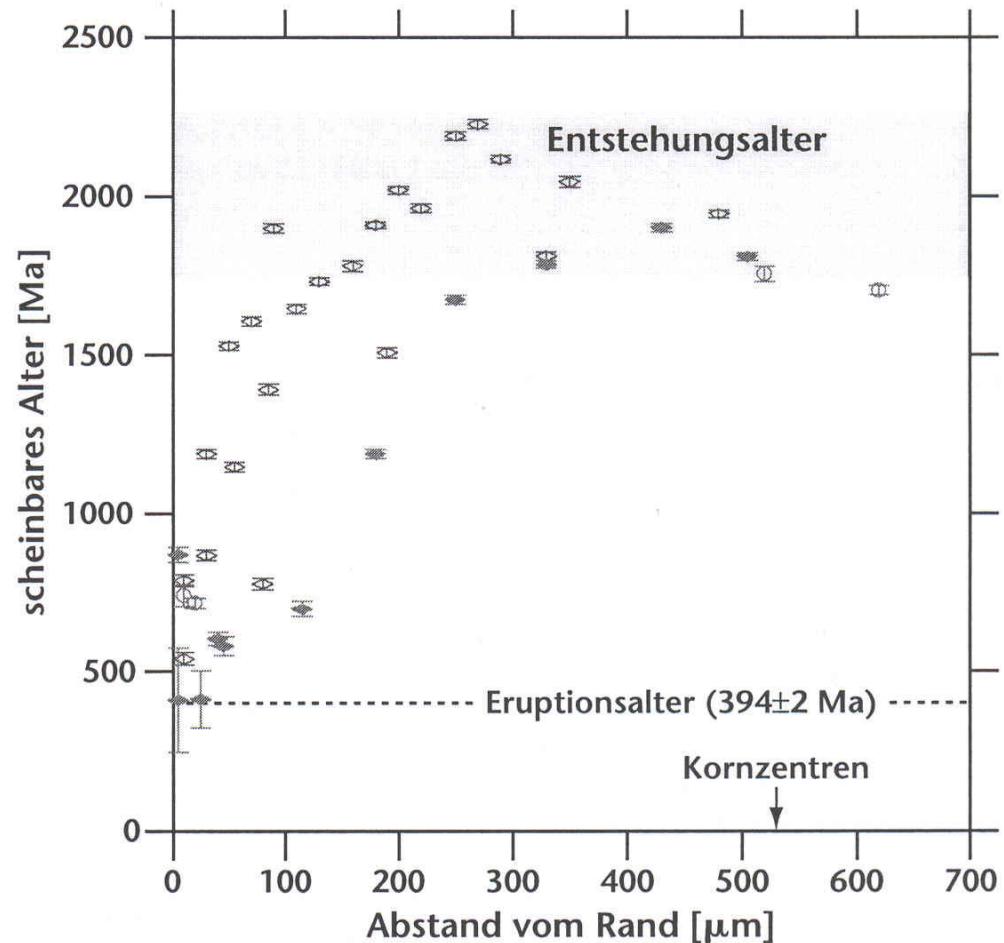
← Age of the kimberlite

# $^{40}\text{Ar}$ - $^{39}\text{Ar}$ dating

Excess (inherited) argon

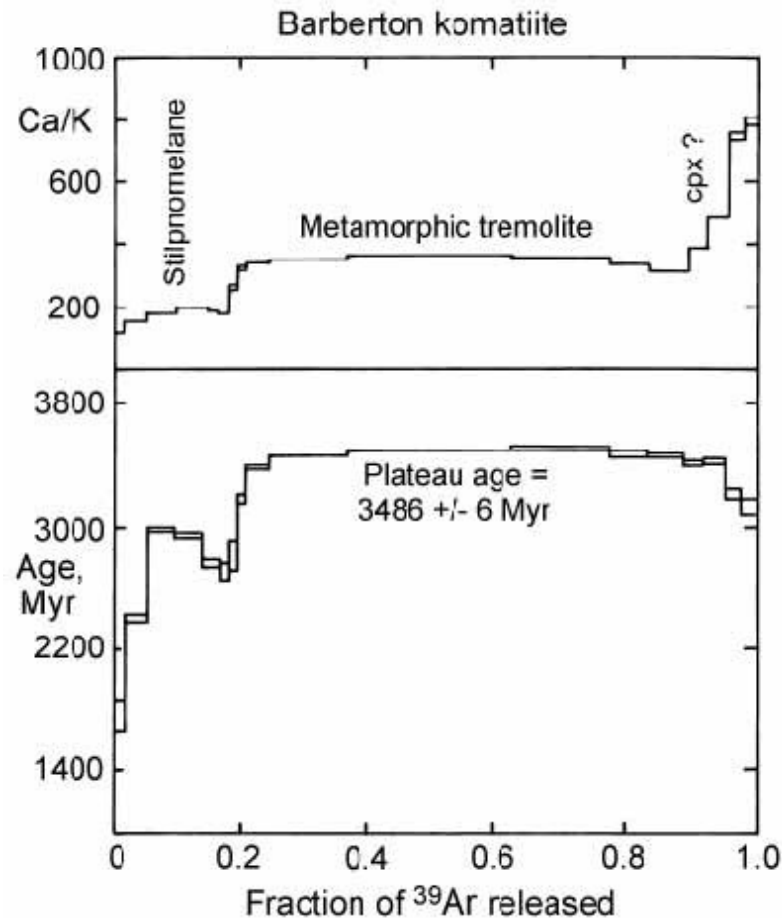
Apparent  $^{40}\text{Ar}/^{39}\text{Ar}$  ages of different phlogopite samples from a crustal xenolith enclosed in a lamprophyre dike

(from G.Stosch, textbook)



# $^{40}\text{Ar}$ - $^{39}\text{Ar}$ dating

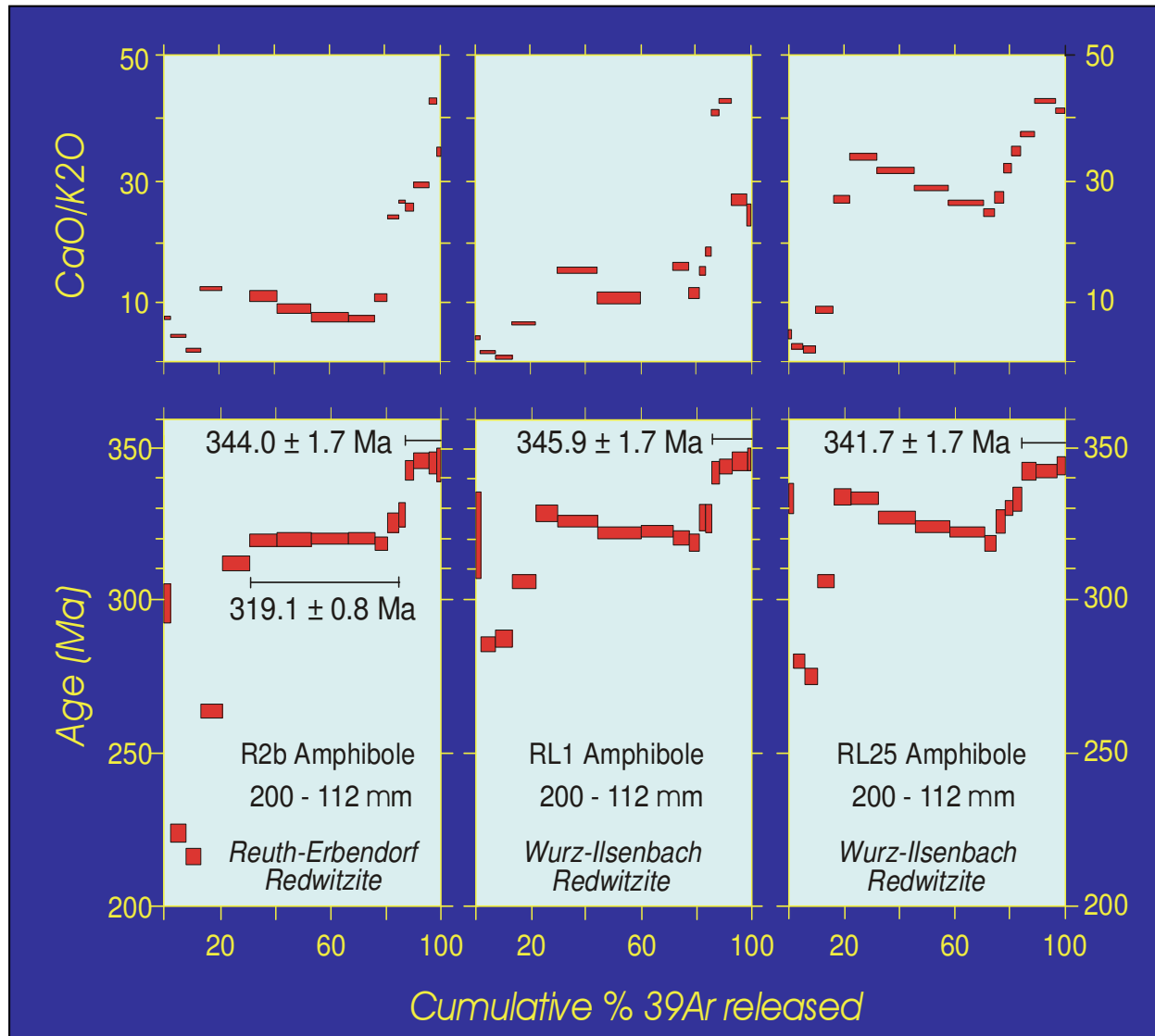
## Presence of different mineral phases

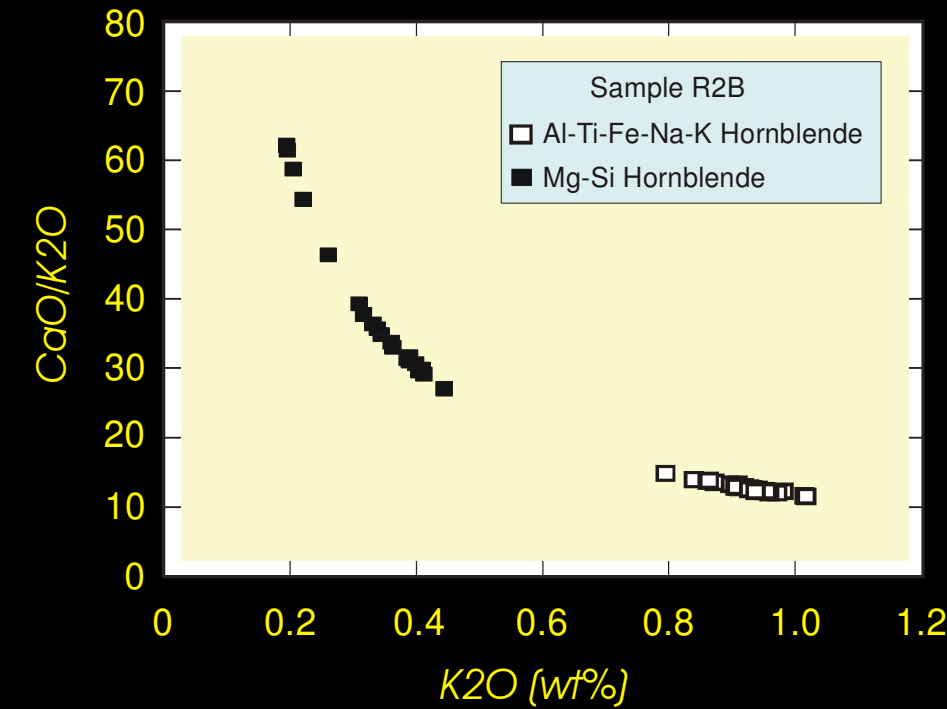
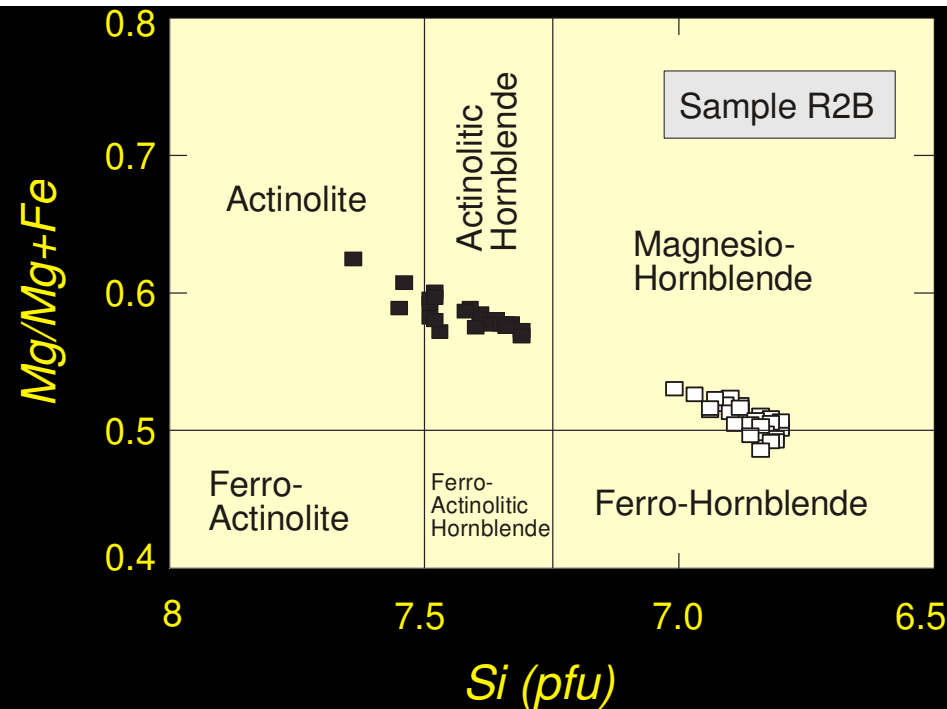
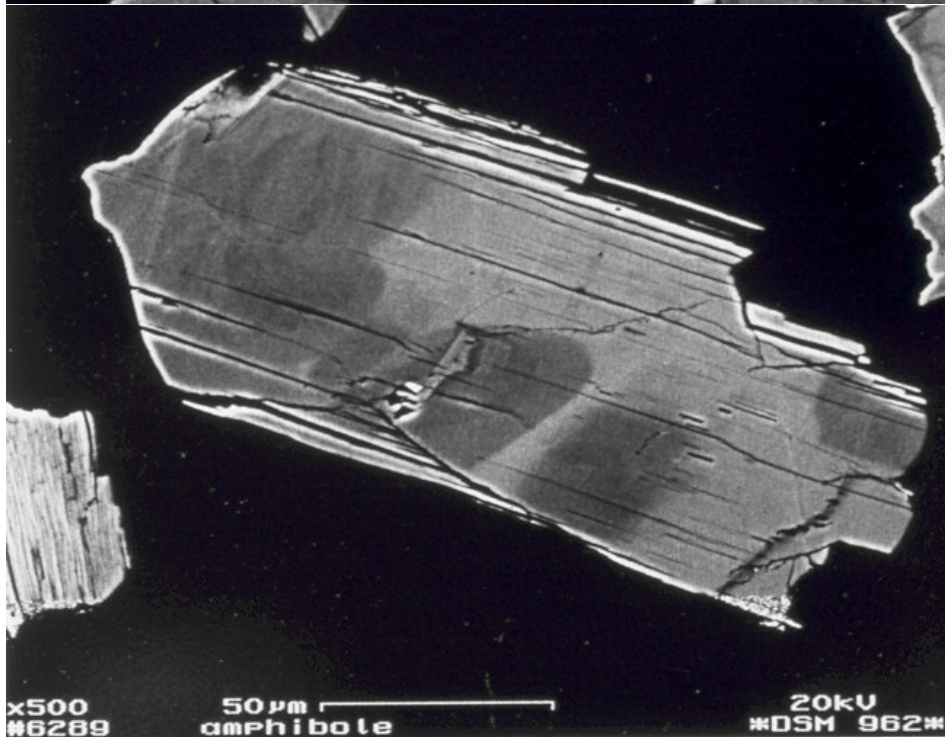
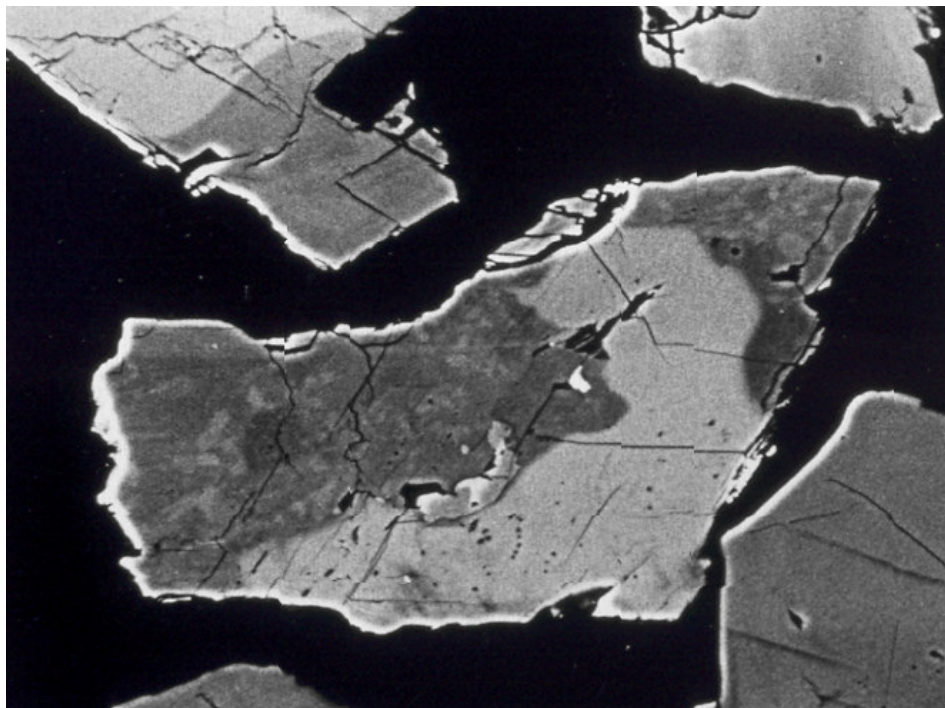


Age spectrum and Ca/K spectrum from Barberton komatiite. Mineral phases responsible for gas releases are identified. After Lopez Martinez *et al.* (1984).

# $^{40}\text{Ar}$ - $^{39}\text{Ar}$ dating

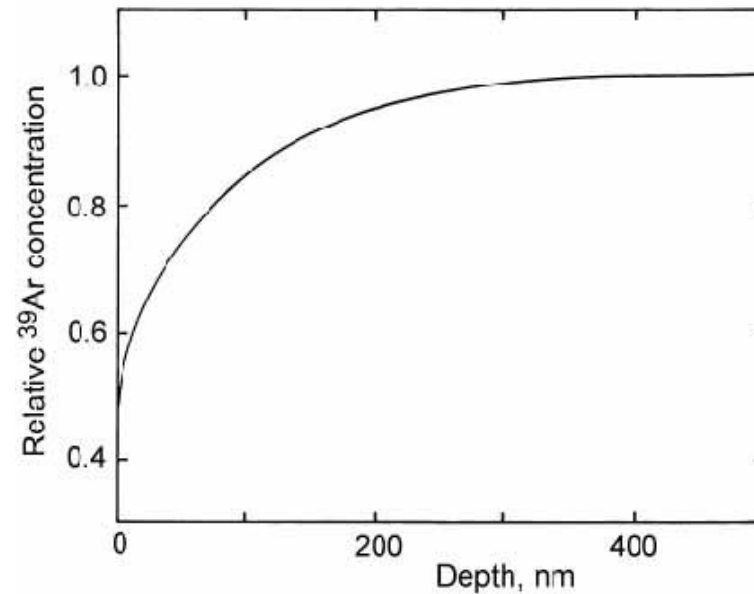
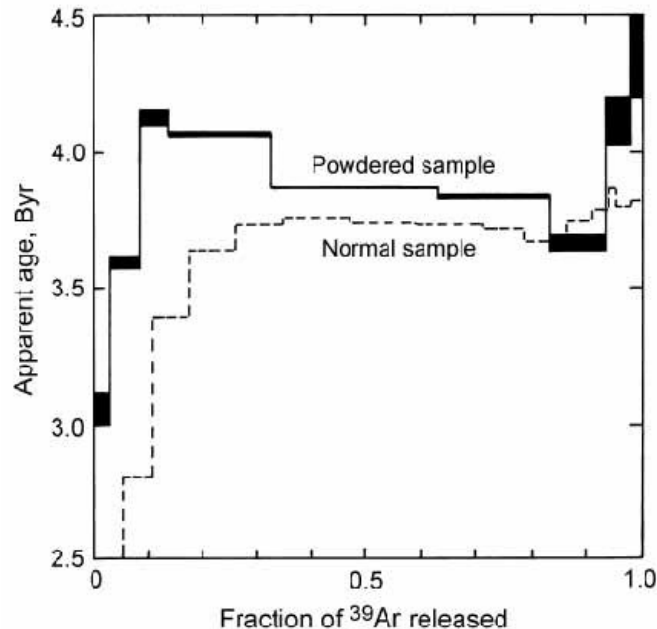
Presence of different mineral phases





# $^{40}\text{Ar}$ - $^{39}\text{Ar}$ dating

## Loss of $^{39}\text{Ar}$ by recoil

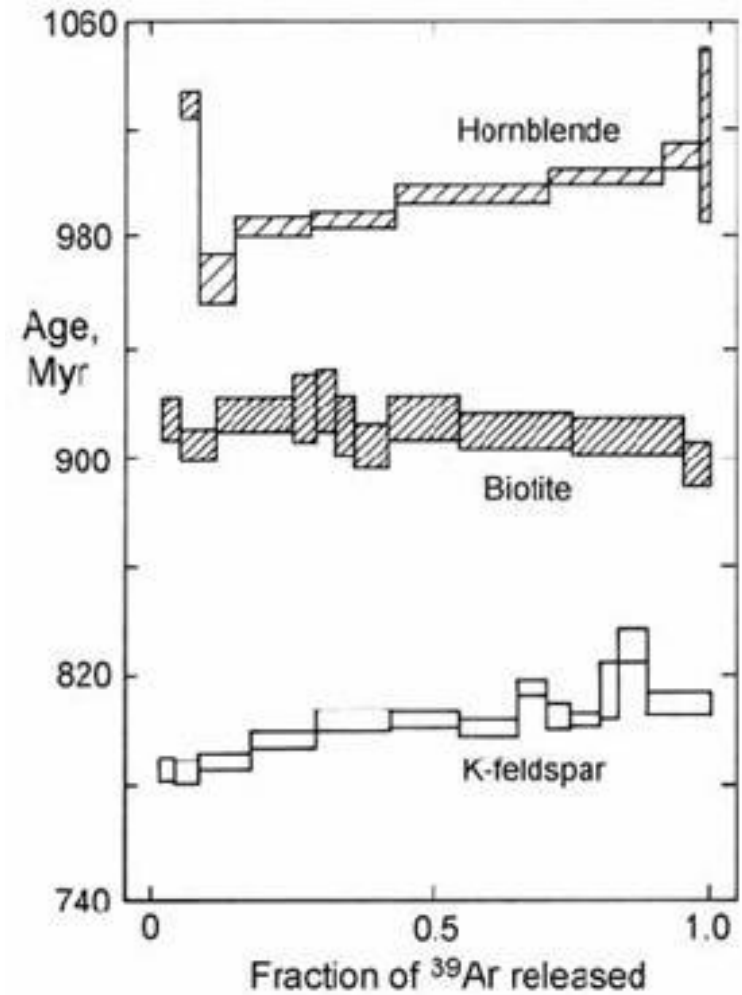
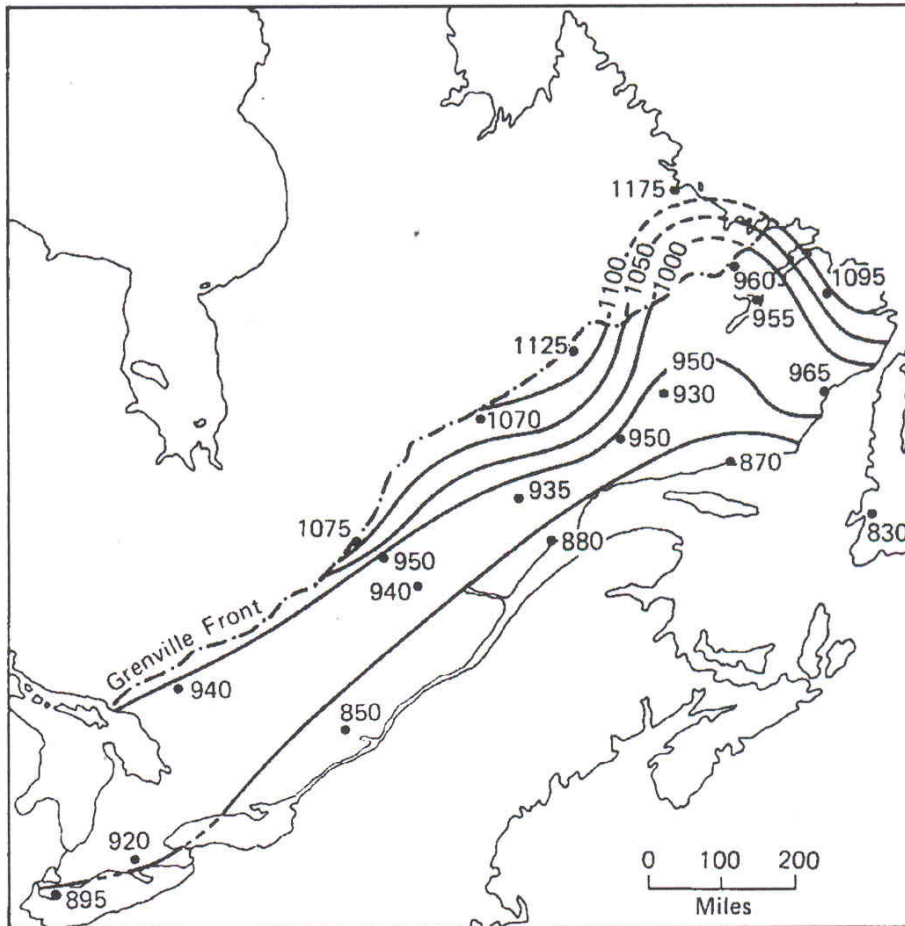


Effect of fine crushing on a  $^{40}\text{Ar}^*/^{39}\text{Ar}$  age spectrum, due to  $^{39}\text{Ar}$  recoil. Dashed profile = analysed rock chip of a lunar mare basalt. Solid profile = similar sample activated after fine powdering. After Turner & Cadogan (1974).

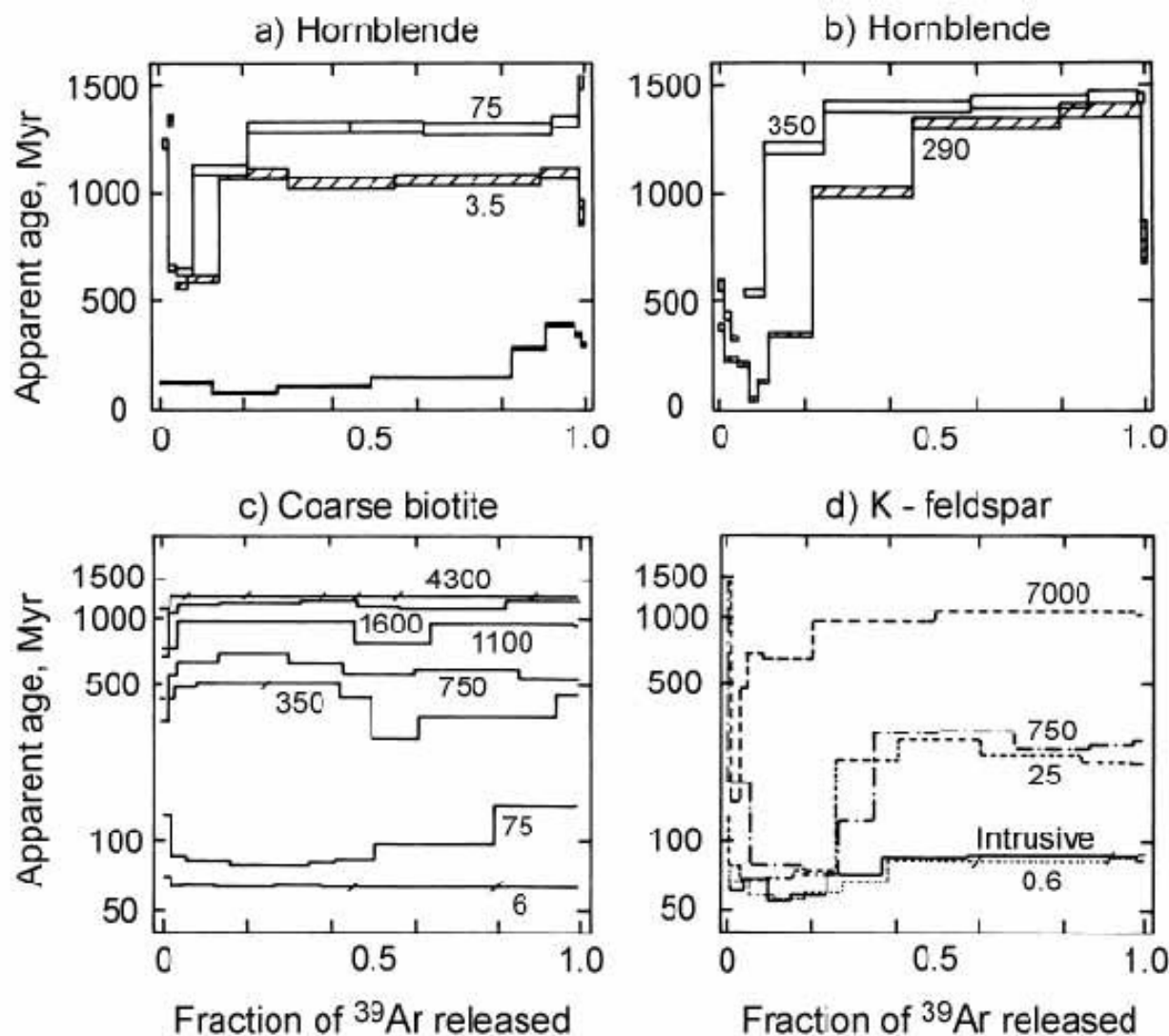
Plot showing calculated drop in  $^{39}\text{Ar}$  concentration at the surface of a K-bearing mineral due to recoil, in response to bombardment with an isotropic neutron flux. After Turner & Cadogan (1974).

# $^{40}\text{Ar}$ - $^{39}\text{Ar}$ dating

Cooling ages of the Grenville province, eastern Canada



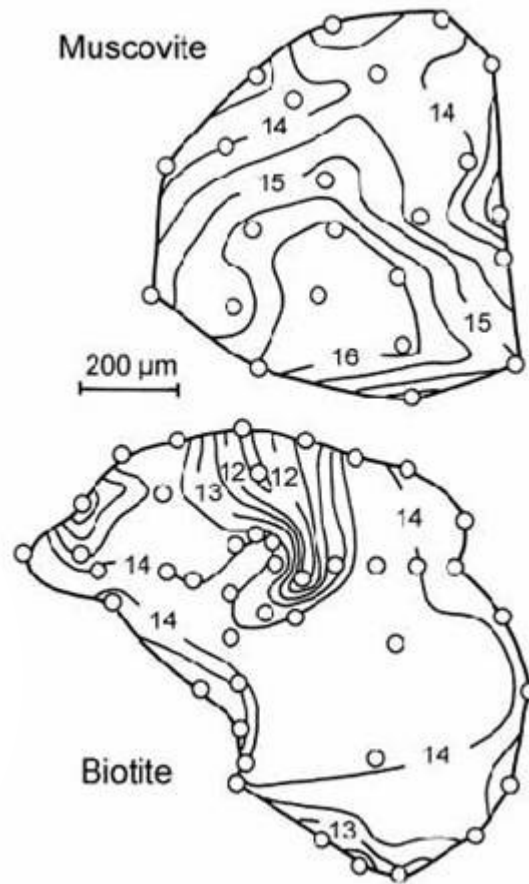
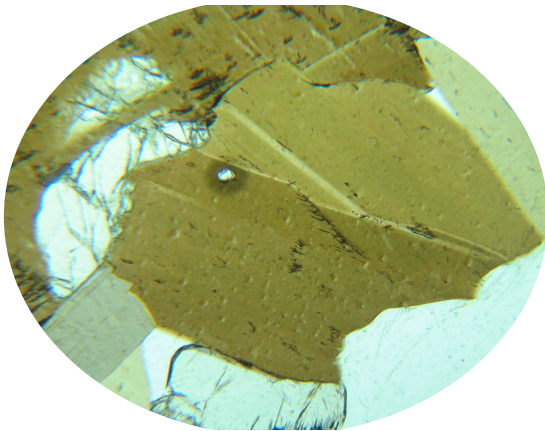
# $^{40}\text{Ar}$ - $^{39}\text{Ar}$ dating



Ar-Ar age spectrum plots for mineral phases at different distances from the **Eldora stock**. Figures beside age spectra indicate distances in m. a), b) hornblende, c) biotite, d) K-feldspar. Release steps with identical ages are separated by slashes. After Berger (1975).

# $^{40}\text{Ar}$ - $^{39}\text{Ar}$ dating

## Other developments: laser spot dating



From Dickin 2005: Rad Iso Geol