#### 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

#### **Eldora stock**

apparent K-Ar mineral ages against outward distance from the contact of the 60 Myr-old Eldora stock, Boulder, Colorado



Hart (1964)

**Diffusion** is the net movement of molecules or atoms from a region of higher concentration (or high chemical potential) to a region of lower concentration (or low chemical potential).



diffusion laws derived by Adolf Fick in 1855 known as **Fick's laws of diffusion** 

#### **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 <u>activation energy</u>

## **Arrhenius equation**

$$D = D_0 \times e^{-E_a/RT} \rightarrow InD = InD_0 - E_a/RT$$

$$y = b + mx$$

- D = diffusion coefficient,
- $D_0$  = diffusion coefficient at infinite T (for T  $\rightarrow \infty$ )
- $E_A$  = activation energy,
- $R = gas constant in J K^{-1}mol^{-1}$ ,
- 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 different temperatures What is the activation energy for the reaction?

$T(^{O}C)$	D				,
$I(\mathbf{C})$	D	D	T(K)	1/T	In <i>D</i>
747	$4.23^{-16}$	4.23 <sup>-16</sup>	1020		
791	$1.55^{-15}$	<b>1.55</b> <sup>-15</sup>	1064		
838	3 15-15	<b>3.45</b> <sup>-15</sup>	1111		
030	5.45	2.09-14	1163		
890	$2.09^{-14}$				

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

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

T(°C)	D	D	T(K)	1/T	ln <i>D</i>
747	$4.23^{-16}$	4.23 <sup>-16</sup>	1020	0,000980	-35,4
791	$1.55^{-15}$	<b>1.55</b> <sup>-15</sup>	1064	0,000940	-34,1
020	2 15-15	3.45 <sup>-15</sup>	1111	0,000900	-33,3
838	3.43	2.09-14	1163	0,000860	-31,5
890	$2.09^{-14}$				

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

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

 $\ln D = \ln D_0 - 1000^* E_a / RT$ Using y = mx + bm = slope and -31 slope m =  $-E_a/R$  $-E_a = mR$ -32 Slope m = -31148-33 (from graph) In(D) with R = 0.00831 kJ/mol K-34 -35  $-E_a = -31148 \times 8.31 \times 10^{-3} \text{ kJ/mol}$ -36 Activation energy: 0.82 0.86 0.90 0.94 0.98  $E_a = 259 \text{ kJ/mol}$  $10^{3}/T(K)$ 

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

- Diffusivity is directly proportional to temperature; weakly dependent on pressure
- Arrhenius equation is:  $D = D_0 exp(-E/RT)$
- Where D<sub>0</sub> 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<sup>-29</sup> m<sup>2</sup>/s to 10<sup>-8</sup> m<sup>2</sup>/s.



Diffusion is thermally activated and obeys an Arrhenius law



Calculation of closure temperatures E/R  $T_c =$  $ART_{C}^{2}(D_{0}/a^{2})$ E dT/dtDodson 1973 E = activation energy $D_0 = Sr$  diffusion factor R = gas constant  $T_c = closure temperature$ A = anisotropy factor a = particle radius dT/dt = cooling rateThe equation is solved by assuming a value

for  $T_C$  and solving for  $T_C$  iteratively

#### **Exercise 6**

Weight of sample and weight of spike

### Cooling curve for a Grennville terrane in Canada



Berger & York, 1981

#### Cooling curve for a Grennville terrane in Canada



Berger & York, 1981

#### **Closure Temperature**

the temperature at which a cooling mineral can no longer exchange isotopes with it's surroundings

Mineral	Method	T (°C)
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.

- Mineral forms and cools
  - Mineral at time of formation has K but no Ar
  - After mineral has formed or cooled to certain temperature (→ closure temperature) its radiometric clock starts and <sup>40</sup>Ar\* is accumulated through decay of <sup>40</sup>K



## **Potassium-Argon Dating** • ${}^{40}\text{K}{}^{40}\text{Ar} \rightarrow \text{half-life} = 1.3 \text{ billion years}$



#### 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 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 <sup>40</sup>Ar/<sup>39</sup>Ar Method, 2nd Edn. Oxford Univ. Press, 269 pp.

Kelly, S. (2002) K-Ar and Ar-Ar Dating. Reviews in Mineralogy and Geochemistry (2002) 47 (1): 785-818

 $40K + e^{-} \rightarrow 40Ar$ 

40

Ar

22

Potassium (K) naturally occurs in 3 isotopes:



 $^{40}$ K/K ratio constant at a given time; present day  $^{40}$ K/K = 0.0001167

#### <sup>40</sup>K is a radioactive isotope of potassium

- Half-life 1.28 Ga
- <sup>40</sup>K (the radioactive isotope converts to Ca and Ar)
- Measure the ratio of Argon to Potassium
  - provides age information



- 88.8% machen einen β<sup>-</sup>-Zerfall in den Grundzustand von <sup>40</sup>Ca (Zerfallsenergie 1.32 MeV)
- ② 0.16% machen einen Elektroneneinfang in den Grundzustand von <sup>40</sup>Ar (Zerfallsenergie 1.51 MeV)
- ③ 0.001% machen einen β<sup>+</sup>-Zerfall in einen angeregten Zustand von <sup>40</sup>Ar (Zerfallsenergie 0.49 MeV)
- ④ 11.0% machen einen Elektroneneinfang in einen angeregten Zustand
  <sup>40</sup>Ar (Zerfallsenergie 0.05 MeV)
- ⑤ ⑥ Zerfall der angeregten Zustände von <sup>40</sup>Ar in den Grundzustand unter γ-Emission

## **Electron capture**

parent nucleus captures one of its orbital electrons and emit a neutrino

Most commonly, it is a K-shell electron which is captured, and this is referred to as K-capture



Mutter

nuklid

**β**+



- 88.8% machen einen β<sup>-</sup>-Zerfall in den Grundzustand von <sup>40</sup>Ca (Zerfallsenergie 1.32 MeV)
- ② 0.16% machen einen Elektroneneinfang in den Grundzustand von <sup>40</sup>Ar (Zerfallsenergie 1.51 MeV)
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- ⑤ ⑥ Zerfall der angeregten Zustände von <sup>40</sup>Ar in den Grundzustand unter γ-Emission

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

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

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

$$t = \frac{1}{\lambda} \ln \left[ \frac{{}^{40}\text{A}r^{*}}{{}^{40}\text{K}} \left( \frac{\lambda}{\lambda_{e}} \right) + 1 \right]$$

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

$$\begin{split} \lambda_{\rm e} &= 0.581 \ \text{x} \ 10^{-10} \text{y}^{-1} \\ \lambda_{\beta} &= 4.962 \ \text{x} \ 10^{-10} \text{y}^{-1} \\ \lambda &= (0.581 + 4.962) \ \text{x} \ 10^{-10} = 5.543 \ \text{x} \ 10^{-10} \text{y}^{-1} \end{split}$$

#### **Exercise 7**

Example: K = 8.378%, <sup>40</sup>Ar\* = 0.3305 ppm

Calculate the <sup>40</sup>Ar\*/<sup>40</sup>K ratio



Example: K = 8.378%, <sup>40</sup>Ar\* = 0.3305 ppm

Calculate <sup>40</sup>Ar\*/<sup>40</sup>K ratio

=

0.3305 x 39.098304 x A

= 0.03307

8.378 x 10<sup>4</sup> x 0.0001167 x 39.9623 x A

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

39.098304 =atomic weight of potassium 39.9623 =atomic weight of <sup>40</sup>Ar

Example: K = 8.378%, <sup>40</sup>Ar\* = 0.3305 ppm

Calculate <sup>40</sup>Ar\*/<sup>40</sup>K ratio

=

0.3305 x 39.098304 x A

= 0.03307

8.378 x 10<sup>4</sup> x 0.0001167 x 39.9623 x A

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

39.098304 =atomic weight of potassium 39.9623 =atomic weight of <sup>40</sup>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)



- General application
  - Crystals or glassy matrix from igneous rocks, minerals from metamorphic rocks and minerals from sedimentary rocks
  - Frequently dated material
    - Basalt
    - Tephra (Volcanic Ash)
    - Pumice
    - Mica (biotite, muscovite), amphibol, K-feldspar
    - glaucony, clay minerals (illite)

- 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% of the <sup>40</sup>K decays to <sup>40</sup>Ar\* by electron capture (89% of <sup>40</sup>K decays via β-minus-decay to <sup>40</sup>Ca)
- Ages obtained by this method may not agree with other methods due to Ar loss

#### K-Ar dating does not always give meaningful ages



## Popping rocks



## K-Ca method



#### <sup>40</sup>K-<sup>40</sup>Ca and <sup>40</sup>K-<sup>39</sup>Ar methods





#### K-Ar analyses of biotite

<sup>40</sup>Ar-<sup>39</sup>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

Stepwise heating technique

Dating of small samples; also: in situ laser dating

Irradiation of K-bearing sample in nuclear reactor

#### Interfering reactions



Argon Produced	Calcium	Potassium	Argon	Chlorine
<sup>36</sup> Ar	<sup>40</sup> Ca			
<sup>37</sup> Ar	<sup>40</sup> Ca	<sup>39</sup> K	<sup>36</sup> Ar	
<sup>38</sup> Ar	<sup>42</sup> Ca	<sup>39</sup> K <sup>41</sup> K	<sup>40</sup> Ar	<sup>37</sup> Cl
39Ar	<sup>42</sup> Ca <sup>43</sup> Ca	<sup>39</sup> K <sup>40</sup> K	<sup>38</sup> Ar <sup>40</sup> Ar	
<sup>40</sup> Ar	<sup>43</sup> Ca <sup>44</sup> Ca	<sup>40</sup> K <sup>41</sup> K		
Beneficial reactions Undesirable reactions				
Insignificant reactions				

Production reaction (heavy arrow) and major interfering reactions (solid) during neutron activation. Dashed reaction to <sup>37</sup>Ar is the interference monitor (Mitchell 1968)

<sup>39</sup>Ar is unstable with half life of 269 years

#### Interfering reactions

Table 3. Interfering reactions on Ca, K, Ar and Cl.

Important interfering reactions are shown in **bold** type. The main <sup>39</sup>Ar-producing reaction is shown with a single border.

Argon isotope	Са	K	Ar	Cl
36 <sub>Ar</sub>	40 <sub>Ca(n,n\alpha)</sub> 36 <sub>Ar</sub>			$^{35}Cl(n,\gamma)^{36}Cl \rightarrow \beta^{-} \rightarrow ^{36}Ar$
37 <sub>Ar</sub>	$40_{Ca(n,\alpha)}37_{Ar}$	<sup>39</sup> K(n,nd) <sup>37</sup> Ar	$36_{Ar(n,\gamma)}37_{Ar}$	
<sup>38</sup> Ar	$42_{Ca(n,n\alpha)}38_{Ar}$	<sup>39</sup> K(n,d) <sup>38</sup> Ar	$^{40}$ Ar(n,nd) $^{38}$ Cl $\rightarrow\beta$ - $\rightarrow$ $^{38}$ Ar	$^{37}Cl(n,\gamma)^{38}Cl \rightarrow \beta^{-} \rightarrow ^{38}Ar$
		$^{41}K(n,\alpha)^{38}Cl \rightarrow \beta^{-} \rightarrow ^{38}Ar$		
<sup>39</sup> Ar	$^{42}Ca(n,\alpha)^{39}Ar$	<sup>39</sup> K(n,p) <sup>39</sup> Ar	$^{38}\mathrm{Ar}(\mathrm{n},\gamma))^{39}\mathrm{Ar}$	
	$^{43}Ca(n,n\alpha)^{39}Ar$	$^{40}$ K(n,d) $^{39}$ Ar	$^{40}\text{Ar(n,d)}^{39}\text{Cl}\rightarrow\beta^{-}\rightarrow^{39}\text{Ar}$	
$40_{\rm Ar}$	$^{43}Ca(n,\alpha)^{40}Ar$	<sup>40</sup> K(n,p) <sup>40</sup> Ar		
	$^{44}Ca(n,n\alpha)^{40}Ar$	$^{41}K(n,d)^{40}Ar$		

The terminology (a,b) used here refers to nuclear reactions taking place during irradiation where a is the incident particle and b is the resulting emission. The terms are n=neutron, p = proton, d = deutron,  $\alpha = and alpha particle$ ,  $\gamma = a$  gamma particle and  $\beta^- = a$  positron.

#### <sup>40</sup>Ar-<sup>39</sup>Ar dating Principles

Number of <sup>39</sup>Ar atoms formed in the sample in the reactor:

<sup>39</sup>Ar = <sup>39</sup>K 
$$\Delta$$
T  $\int \phi(\varepsilon)\sigma(\varepsilon) d\varepsilon$ 

 $\Delta T$  = length of irradiation

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

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

 $\epsilon = energy$ 

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

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

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

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

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

<sup>40</sup>Ar-<sup>39</sup>Ar dating Flux monitor





**Figure 2.** A Figure for optimizing irradiation parameters, taking account of age and Ca/K. The irradiation parameter is plotted against Age (Ma) and zones of optimum irradiation level are highlighted (after McDougall and Harrison 1999; Turner 1971a).

## Terminology – extraneous argon

**Excess argon** – from fluids or melt inclusions

**Inherited argon** – incorporated from older materials (e.g. lithic fragments in an ignimbrite)

in the simple case, all the non-radiogenic argon is atmospheric:

 ${}^{40}\text{Ar}^{*/39}\text{Ar} = [{}^{40}\text{Ar}^{*/39}\text{Ar}]_{m} - 295.5[{}^{36}\text{Ar}/{}^{39}\text{Ar}]_{m}$ 

#### **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 °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).

#### Data presentation



Ideal <sup>40</sup>Ar/<sup>39</sup>Ar age spectra for two tektite glasses, distinguished by solid and dashed boxes. After York (1984).

#### Argon loss events





<sup>40</sup>Ar/<sup>39</sup>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).

Argon loss events



 $^{40}$ Ar/ $^{39}$ Ar argon release pattern of the Bruderheim meteorite, compared with calculated argon loss profiles from spherical mineral grains formed at 4.5 Byr and disturbed at 0.5 Byr. a) assuming uniform size distribution; b) log-normal size distribution with F = 0.20. After Turner (1968).



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) Kfeldspar. After Berger (1975).

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 °C. After Lanphere and Dalrymple (1976).

— Age of the kimberlite

### <sup>40</sup>Ar-<sup>39</sup>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).

#### <sup>40</sup>Ar-<sup>39</sup>Ar dating Excess (inherited) argon

Apparent <sup>40</sup>Ar/<sup>39</sup>Ar ages of different phlogopite samples from a crustal xenolith enclosed in a lamprophyre dike

(from G.Stosch, textbook)



#### Other developments: laser spot dating



![](_page_52_Figure_3.jpeg)

From Dickin 2005: Rad Iso Geol

![](_page_53_Figure_0.jpeg)

Figure 5. Laser profiles showing the effects of cracks and defects in minerals. (a) Biotite in an argon loss experiment, showing an indentation in the age contours resulting from a crack (Onstott et al. 1991). (b) Muscovite exhibiting young ages along an obvious fracture, shown left to right just below the center of the grain (Hames and Cheney 1997). (c) Biotite from a slowly cooled terrain again showing an indentation resulting from a crack (Hodges et al. 1994). (d) K-feldspar from a deformed sandstone, note that old ages are preserved in the center of this boudinaged grain but close to the boudinage and in the smaller fragment, only younger ages were measured (Reddy et al. 2001).

#### <sup>40</sup>Ar-<sup>39</sup>Ar dating Excess (inherited) argon

![](_page_54_Figure_1.jpeg)

**Figure 8.** Excess argon diffusing into a biotite grain from the Seconda Zona Diorito Kinzigitica (IIDK) in the western Alps, the true cooling age of the biotites samples is around 40 Ma (from Pickles et al. 1997).

![](_page_54_Figure_3.jpeg)

#### <sup>40</sup>Ar-<sup>39</sup>Ar dating Thermochronology

![](_page_55_Figure_1.jpeg)

#### Cooling ages of the Grenville province, eastern Canada

time of uplift & cooling - not the age of metamorphism

![](_page_56_Picture_3.jpeg)

![](_page_57_Figure_0.jpeg)

#### <sup>40</sup>Ar-<sup>39</sup>Ar dating Presence of different mineral phases

![](_page_58_Figure_1.jpeg)

![](_page_59_Figure_0.jpeg)

![](_page_59_Figure_1.jpeg)

![](_page_59_Figure_2.jpeg)

### <sup>40</sup>Ar-<sup>39</sup>Ar dating Loss of <sup>39</sup>Ar by recoil

![](_page_60_Figure_1.jpeg)

![](_page_60_Figure_2.jpeg)

Effect of fine crushing on a  ${}^{40}$ Ar\*/ ${}^{39}$ Ar age spectrum, due to  ${}^{39}$ 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 <sup>39</sup>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).