Introduction to $^{40}Ar/^{39}Ar$ geochronology and thermochronology

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Helsinki,

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Learning Outcomes

- You will have an understanding of:
  - K-Ar decay
  - The difference between K-Ar and $^{40}Ar/^{39}Ar$
  - The age equation
  - How data are collected
  - Sources of error

- You will be able to:
  - Manipulate the age equation
  - Calculate K-Ar ages
  - Calculate J values
  - Calculate $^{40}Ar/^{39}Ar$ ages
  - Plot $^{40}Ar/^{39}Ar$ data

Isotopes of natural Argon

- $^{36}Ar = 0.3364 \pm 0.0006$ %
- $^{38}Ar = 0.0632 \pm 0.0001$ %
- $^{40}Ar = 99.600$ %

Atmosphere is ~1% Ar
Atmospheric $^{40}Ar/^{36}Ar$ ratio is ~298.56 ± 0.31
Lee et al., 2006

Isotopes of natural Potassium

- ^{39}K (stable; 93.2581%)
- ^{40}K (radioactive; 0.0117%)
- ^{41}K (stable; 6.7302%)

The Decay

- ^{40}K half life 1.248×10^9 a
  - ^{40}Ca (β decay, 89.1%)
  - ^{40}K (electron capture, 10.9%)

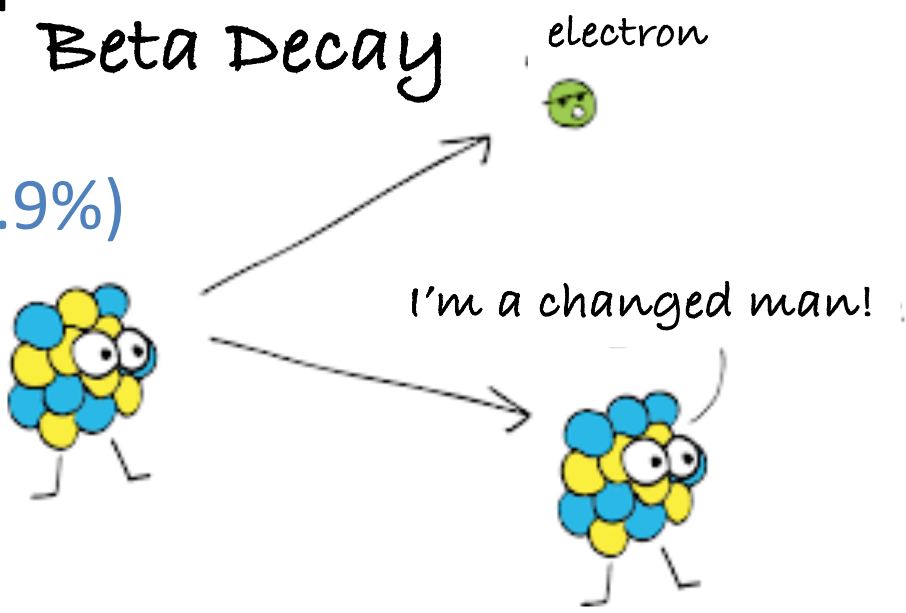


Image: Khan academy

- Only ~0.011% of K consists of ^{40}K, and
- only ~10% of ^{40}K decays to ^{40}Ar

BUT

- K is a major element in numerous rock-forming minerals
- So there is plenty ^{40}Ar to measure

Radiogenic ^{40}Ar ($^{40}Ar^*$)

The amount of ^{40}Ar is proportional to:

- The K concentration
- Time (Age)

- Also have ^{40}Ar in atmosphere
  - Correct using ^{36}Ar
  - Atmospheric $^{40}Ar/^{36}Ar$ = 298.36 ± 0.31

(Lee et al., 2006)

- $^{40}Ar^* = {}^{40}Ar_{total} - {}^{40}Ar_{atm} - {}^{40}Ar_{initial}$

Radiogenic ^{40}Ar

The amount of ^{40}Ar is proportional to:

- The K concentration
- Time (Age)

$$^{40}Ar^{*} = 0.1048\ ^{40}K\ (e^{\lambda t} - 1)$$

Branching ratio as ^{40}K decays to ^{40}Ca (89.5%) and ^{40}Ar (10.5%)

$\lambda = 5.543 \times 10^{-10}\ a^{-1}$

* = radiogenic

t = time

So let's rearrange for t

activity TIME

$$^{40}Ar^* = 0.1048\ ^{40}K\ (e^{\lambda t} - 1)$$

Let’s rearrange for t

$$^{40}Ar^* = 0.1048\ ^{40}K\ (e^{\lambda t} - 1)$$

$$t = \frac{\ln\left[\ (^{40}Ar/0.1048\ ^{40}K) + 1\ \right]}{\lambda}$$

→ the unknowns are ^{40}K and ^{40}Ar

→ What is $1/\lambda$ in Ma? $\lambda = 5.543 \times 10^{-10}\ a^{-1}$

Let's rearrange for t

$$^{40}Ar^* = 0.1048\ ^{40}K\ (e^{\lambda t} - 1)$$

$$t = \frac{\ln [\ (^{40}Ar/0.1048\ ^{40}K) + 1\ ]}{\lambda}$$

→ the unknowns are ^{40}K and ^{40}Ar

→ What is $1/\lambda$ in Ma?

→ 1804.077

Requirements for a K-Ar age

- Constant decay constants
- Sample ^{40}Ar is either all radiogenic OR non-radiogenic ^{40}Ar can be corrected
- Closed system

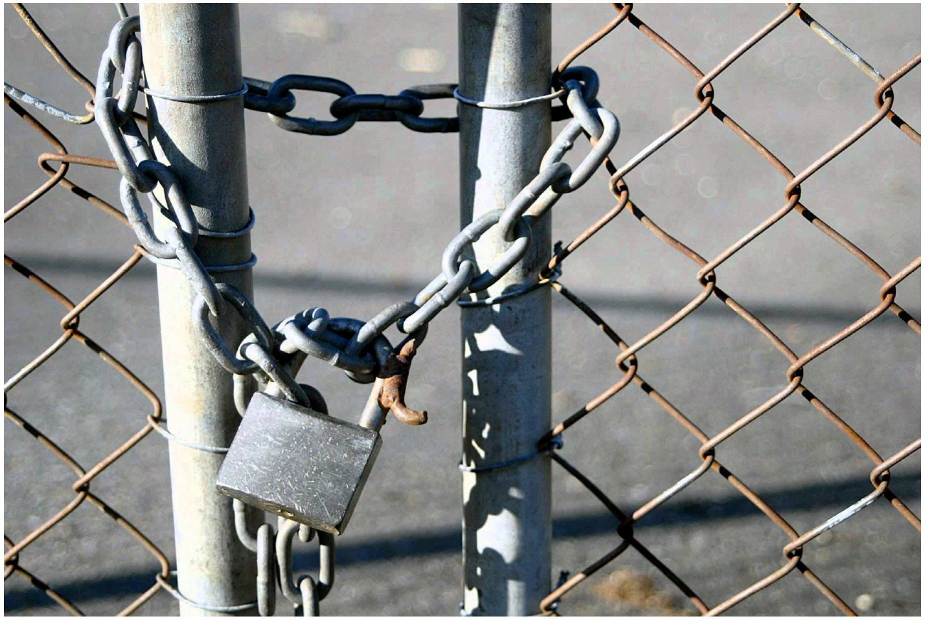
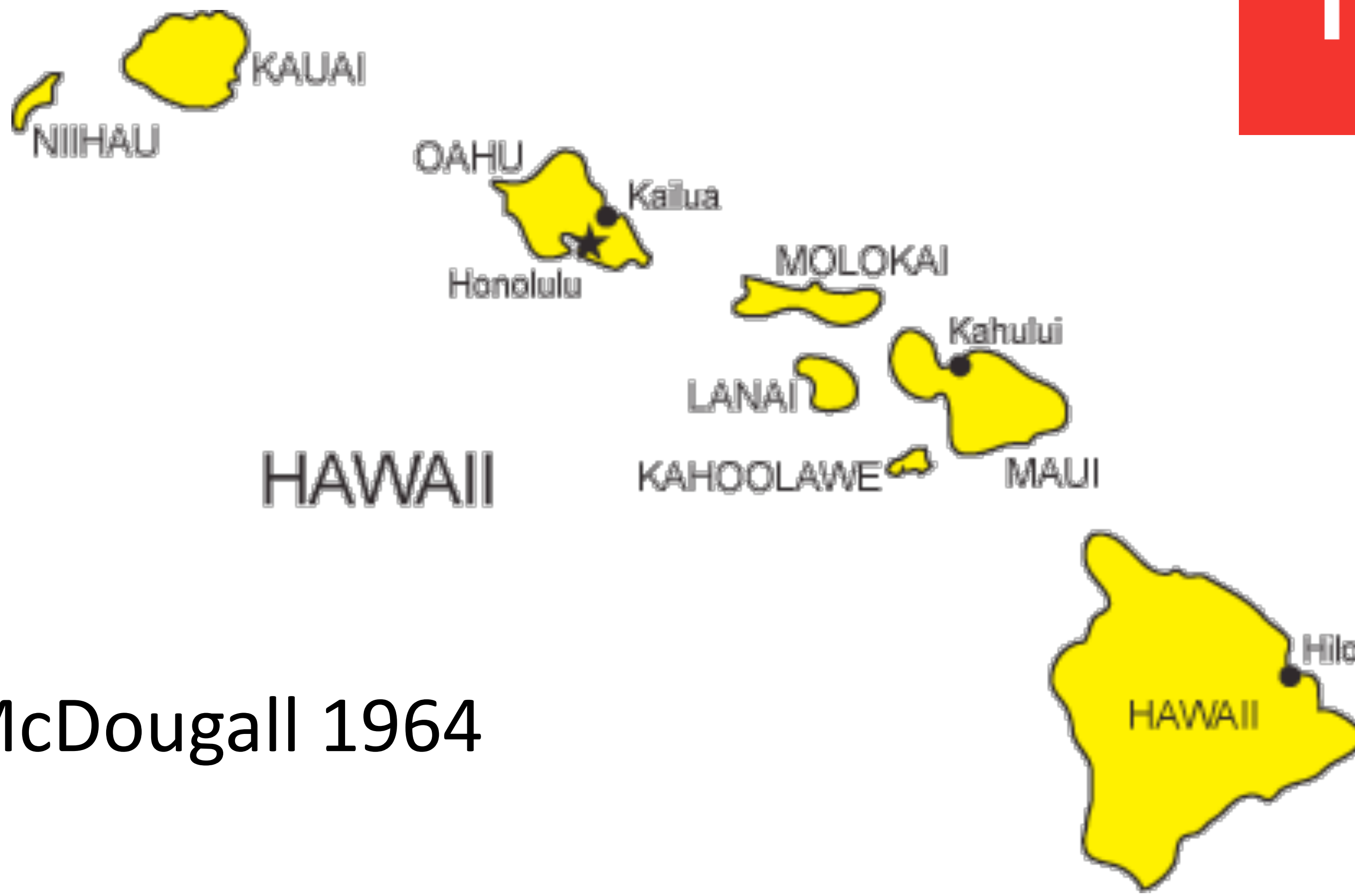


Image: YouTube.com

So let's calculate!

activity TIME



McDougall 1964

$$t = 1804.077 \ln \left[\left({}^{40}Ar / 0.1048\ {}^{40}K \right) + 1 \right]$$

Image: state-maps.org

What is the age range for each island?

Island	$^{40}Ar/^{40}K$ max	$^{40}Ar/^{40}K$ min	Age in Ma?
Kauai	3.34×10^{-4}	2.22×10^{-4}	
W Oahu	2.14×10^{-4}	1.60×10^{-4}	
East Oahu	1.30×10^{-4}	1.50×10^{-4}	
W Molokai	1.08×10^{-4}	--	
E Molokai	8.81×10^{-5}	7.74×10^{-5}	
W Maui	7.68×10^{-5}	6.77×10^{-5}	
E Maui	4.86×10^{-5}	--	

$$t = 1804.077 \ln \left[\left({}^{40}Ar/0.1048\ {}^{40}K \right) + 1 \right]$$

What have you found?

activity TIME

Image: state-maps.org

What have you found?

activity TIME

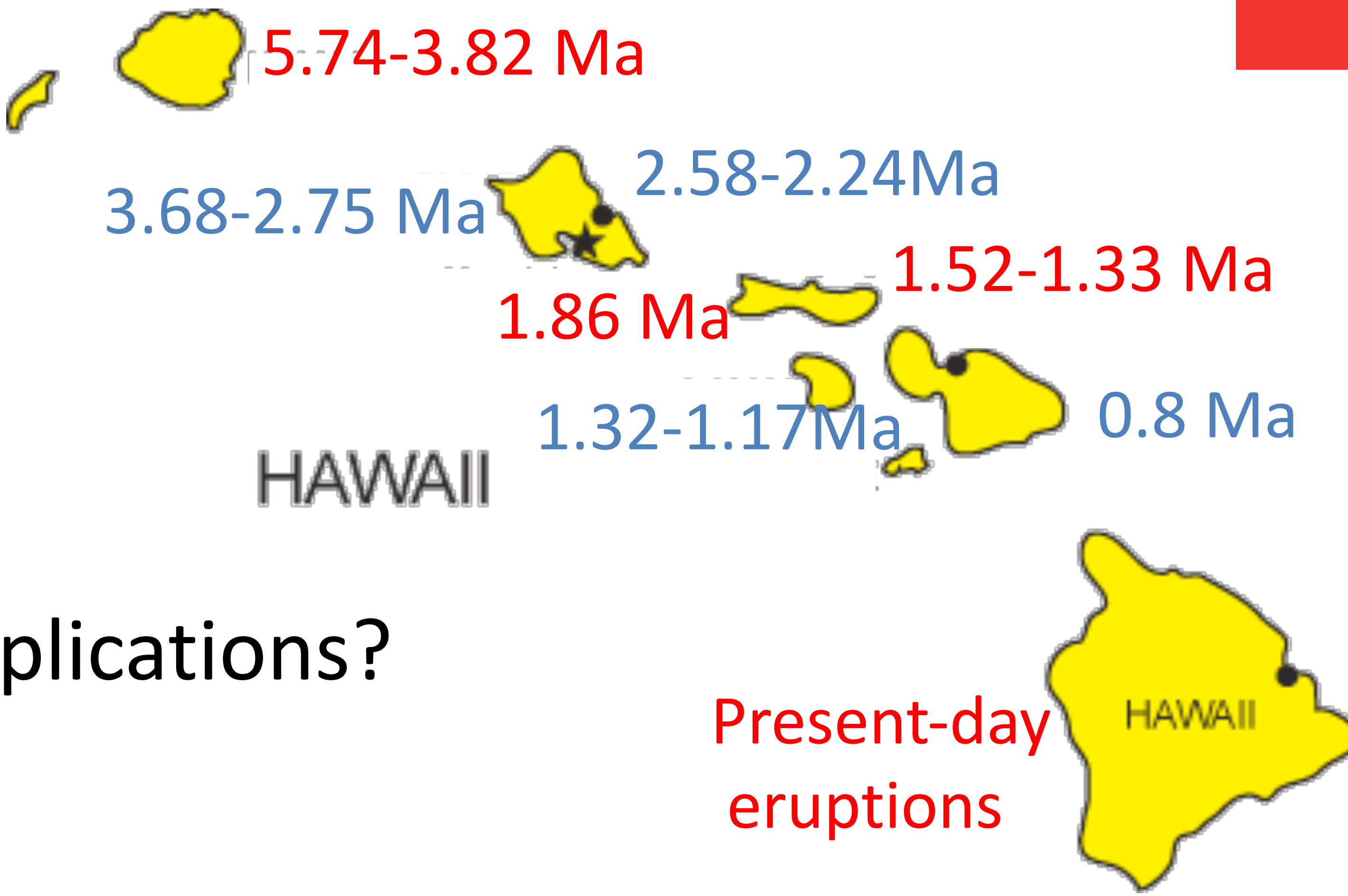


Image: state-maps.org

Implications?

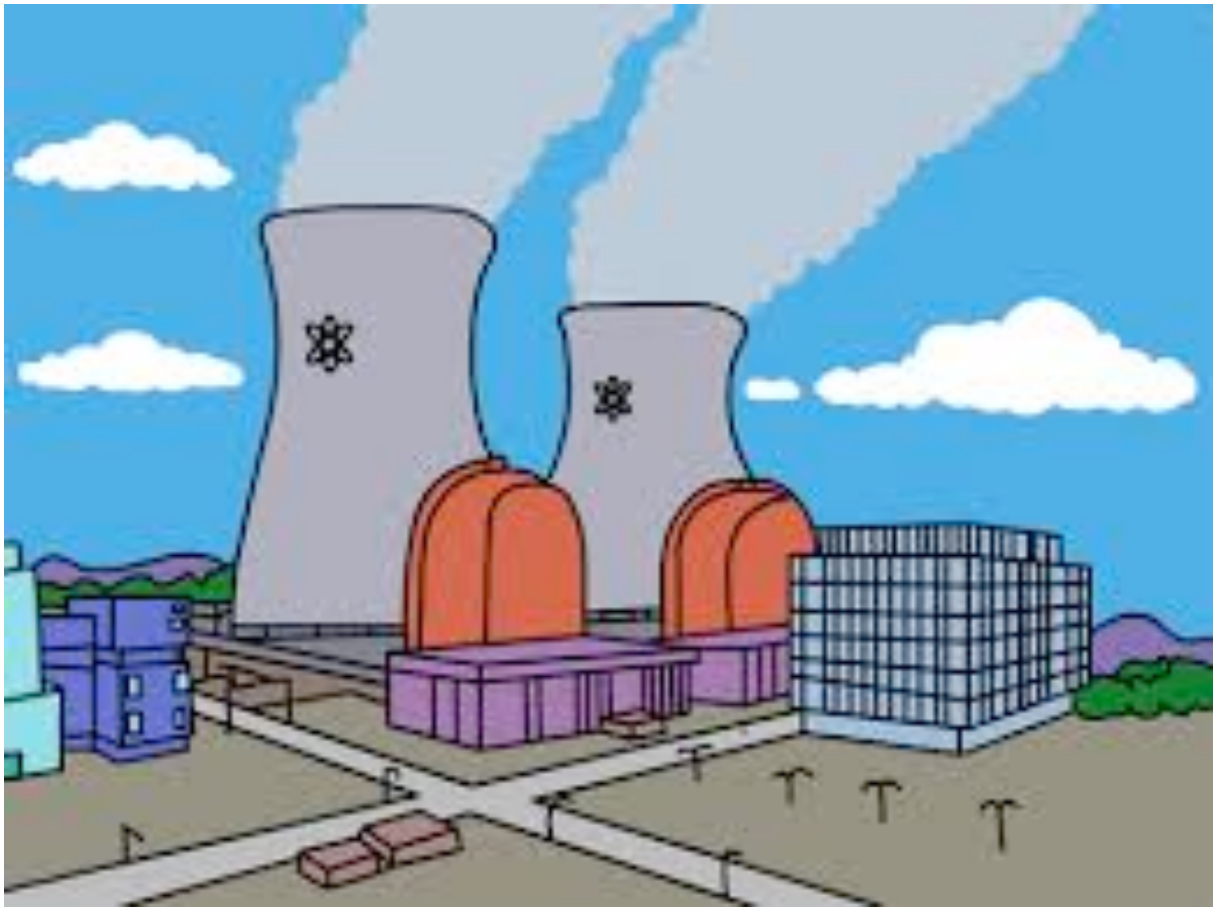
McDougall 1964

K-Ar vs Ar/Ar

Image: Wikipedia

Image: istockphoto.com

Irradiation



$^{39}K \rightarrow {}^{39}Ar$
by neutron bombardment

93.26% of all K is ^{39}K

We can then just measure ^{40}Ar and ^{39}Ar instead of ^{40}Ar and ^{40}K

Image from The Simpsons

Relationship between $^{39}Ar \rightarrow {}^{40}K$?

- Every ^{39}Ar forms from a ^{39}K
- ^{39}K (stable; 93.2581%)
- ^{40}K (radioactive; 0.0117%)

- For every ^{39}K atoms how many ^{40}K?

Relationship between $^{39}Ar \rightarrow {}^{40}K$?

- Every ^{39}Ar forms from a ^{39}K
- ^{39}K (stable; 93.2581%)
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- For every ^{39}K atoms, how many ^{40}K?
  - 0.0001255

Other irradiation products

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

$^{40}Ca(n,n\alpha)^{36}Ar$

$^{40}Ca(n,\alpha)^{37}Ar$

$^{42}Ca(n,\alpha)^{39}Ar$

$^{40}K(n,p)^{40}Ar$

For the 10 MW reactor (LVR-15) in Řež (Czech Republic):

$(^{36}Ar/^{37}Ar)_{Ca} \sim$ 0.000227

$(^{39}Ar/^{37}Ar)_{Ca} \sim$ 0.000602

$(^{40}Ar/^{39}Ar)_{K} \sim$ 0.00183

(slightly variable for different reactor types and irradiation positions within the reactor)

Image from: http://studylib.net/doc/18050406/ar-ar-geo--thermochronology

$^{40}K \rightarrow {}^{39}Ar$?

$$t = \frac{\ln\left[\left({}^{40}Ar / 0.1048\ {}^{40}K \right) + 1 \right]}{\lambda}$$

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

J includes: abundances of K isotopes
branching ratio
irradiation dose

Standard of known age

Image: e-rocks.com

These are irradiated with the samples of unknown age

Image: Pitt.edu

Irradiation factor (J values)

$$J = \frac{e^{(t/1804.077)} - 1}{R}$$

Where R (ratio) = $\dfrac{{}^{40}Ar_{(atm\ corr)}}{{}^{39}Ar}$

And t = age of standard (Ma)

How do we date a rock or mineral?

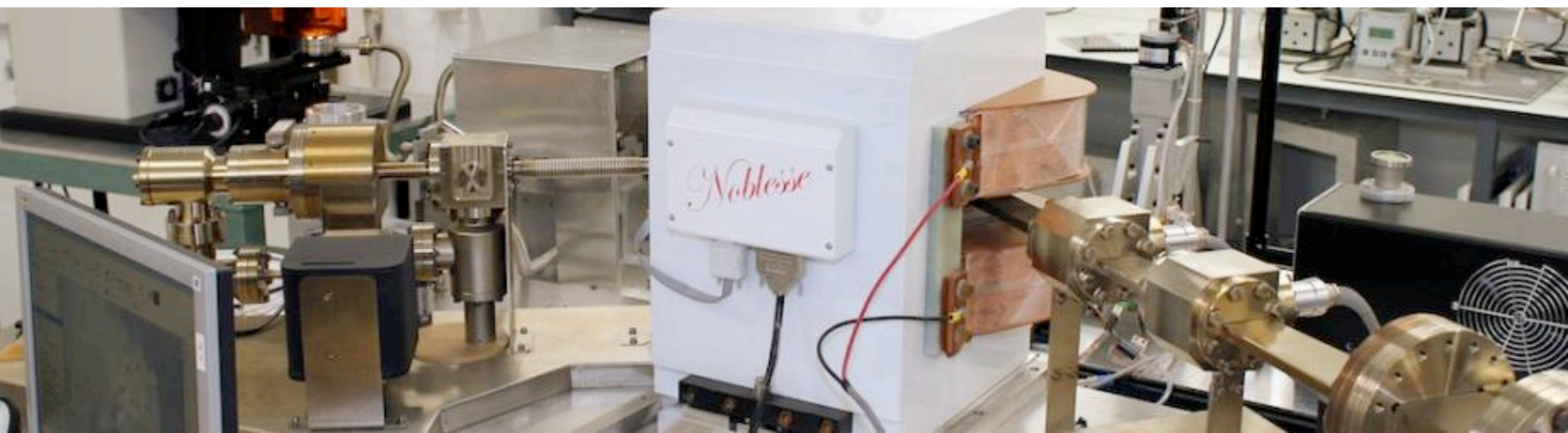
- Pick rock fragments or minerals
- Load with standards
- Irradiate
- Load into mass spec
- Heat/melt/ablate
- Measure ^{36}Ar, ^{37}Ar, ^{38}Ar, ^{39}Ar, ^{40}Ar
- Calculate J value for each sample
- Calculate sample age

Image: ScienceDaily.com

Collecting data

- Step Heating
- Single Grain Fusion
- Laser Ablation
- Crushing

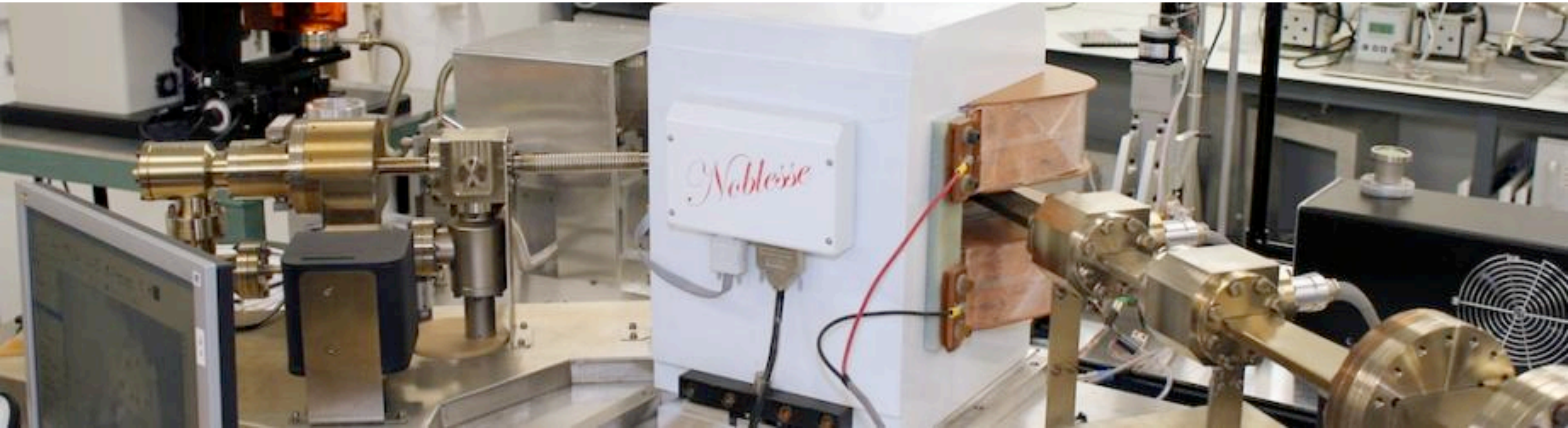
Image: Open.ac.uk



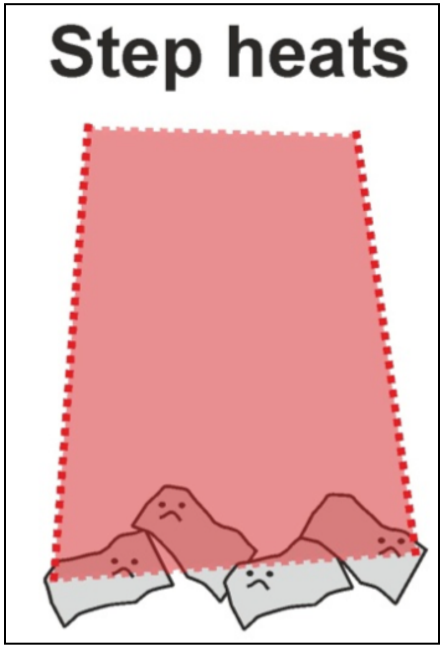
Basically

- Thermal or mechanical release of Ar from sample
- Cleaning gas to remove interferences
- Measurement

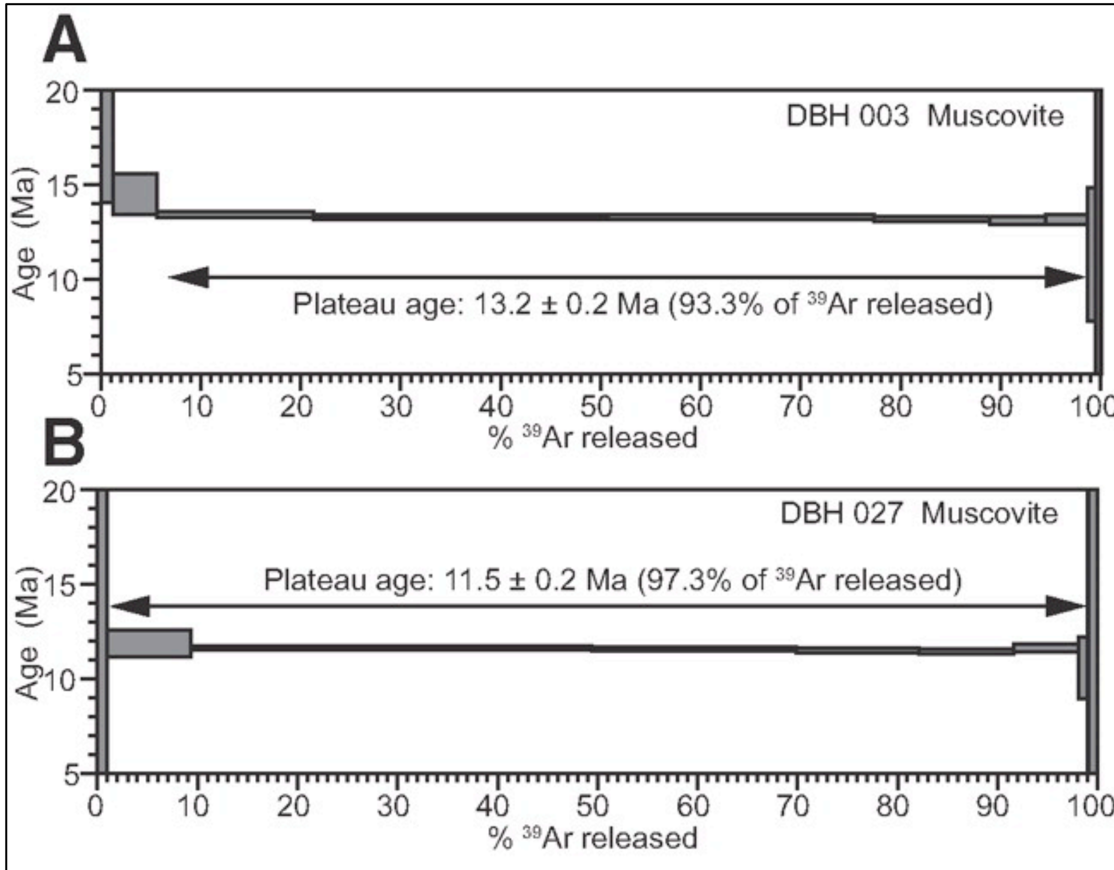
Image: Open.ac.uk



Dating – step heating



Multi-grain;
Single grain



Images: Catherine Mottram; Kellett et al., 2009

Plotting data: Step Heating

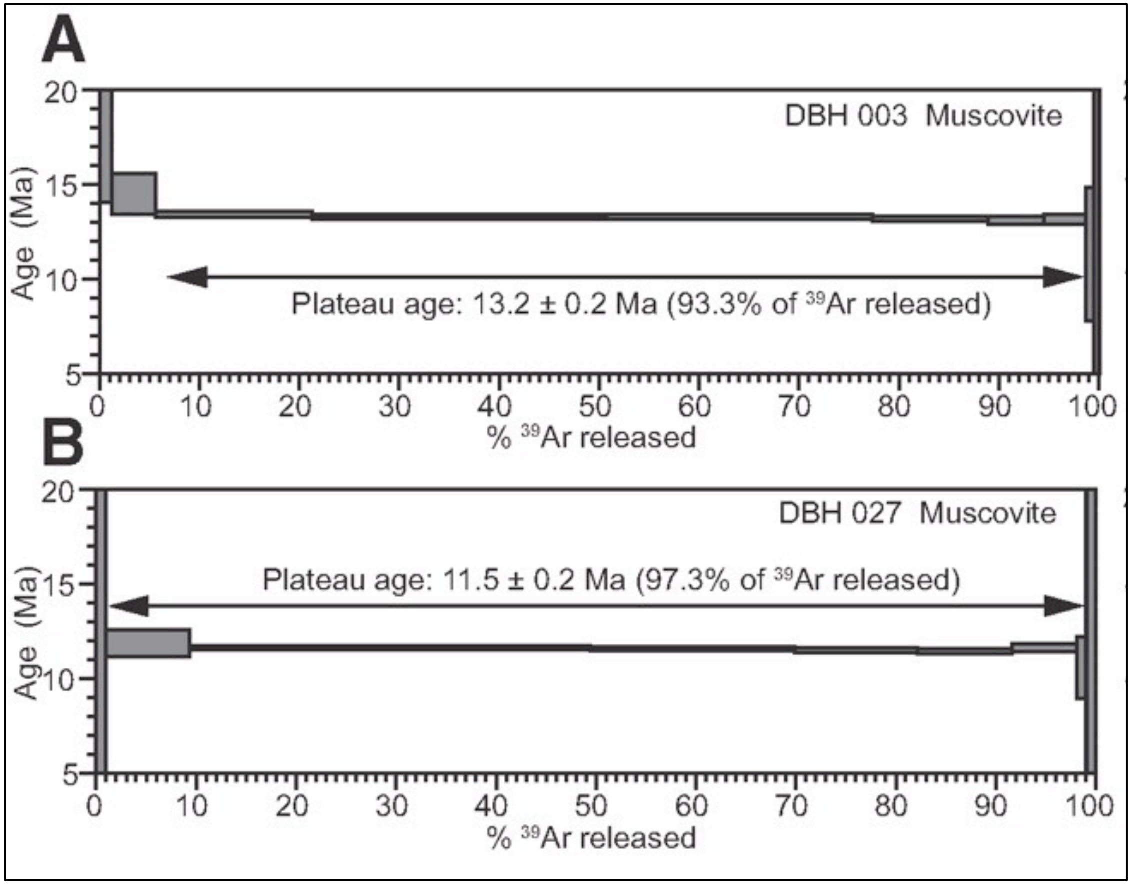


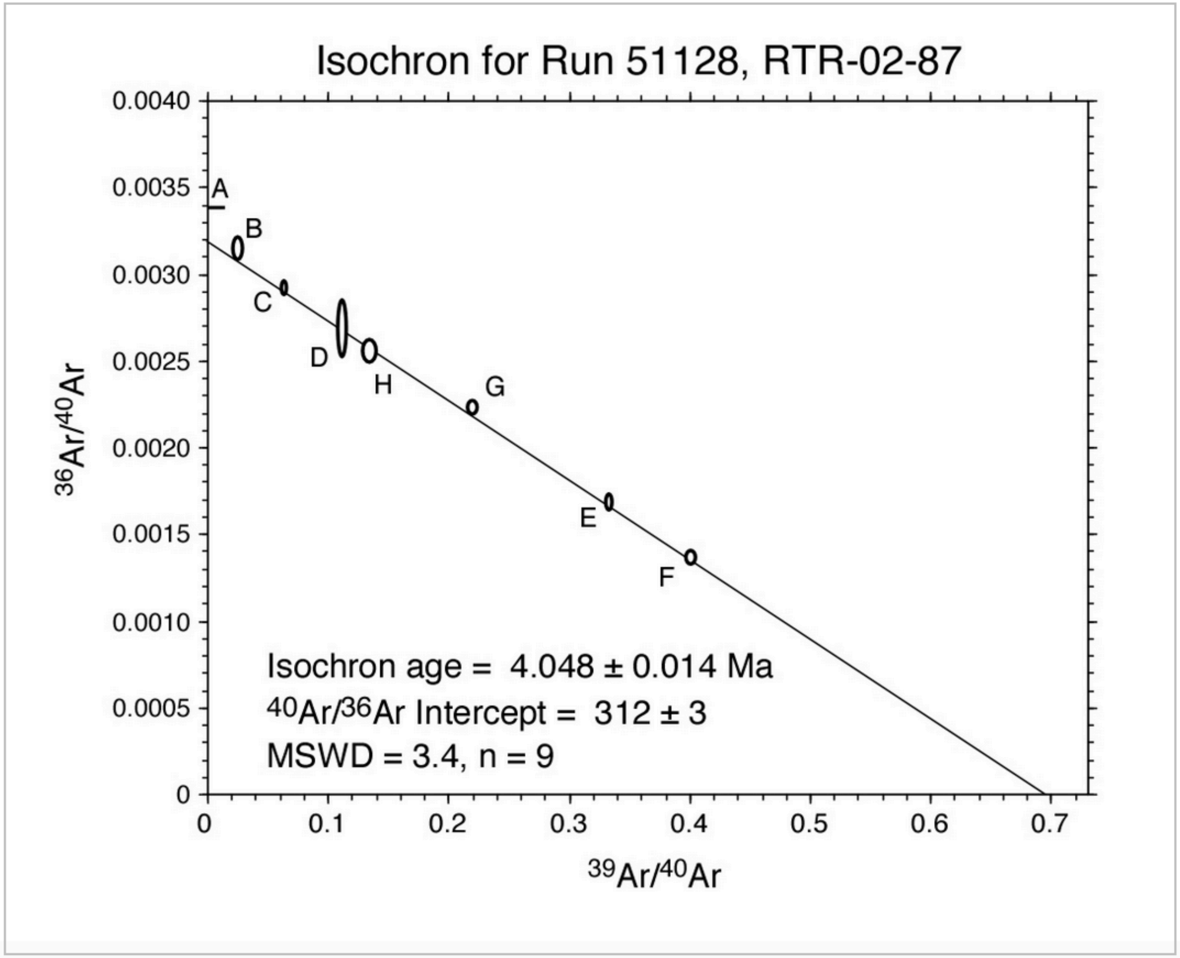
Image: Kellett et al., 2009

Age calculate for each temperature step

Plateau: Fleck et al (1977): 3 or more contiguous steps; > 50% released $^{39}Ar_K$ + overlapping at 2σ

Fit calculated by MSWD

Plotting data: Inverse Isochrons

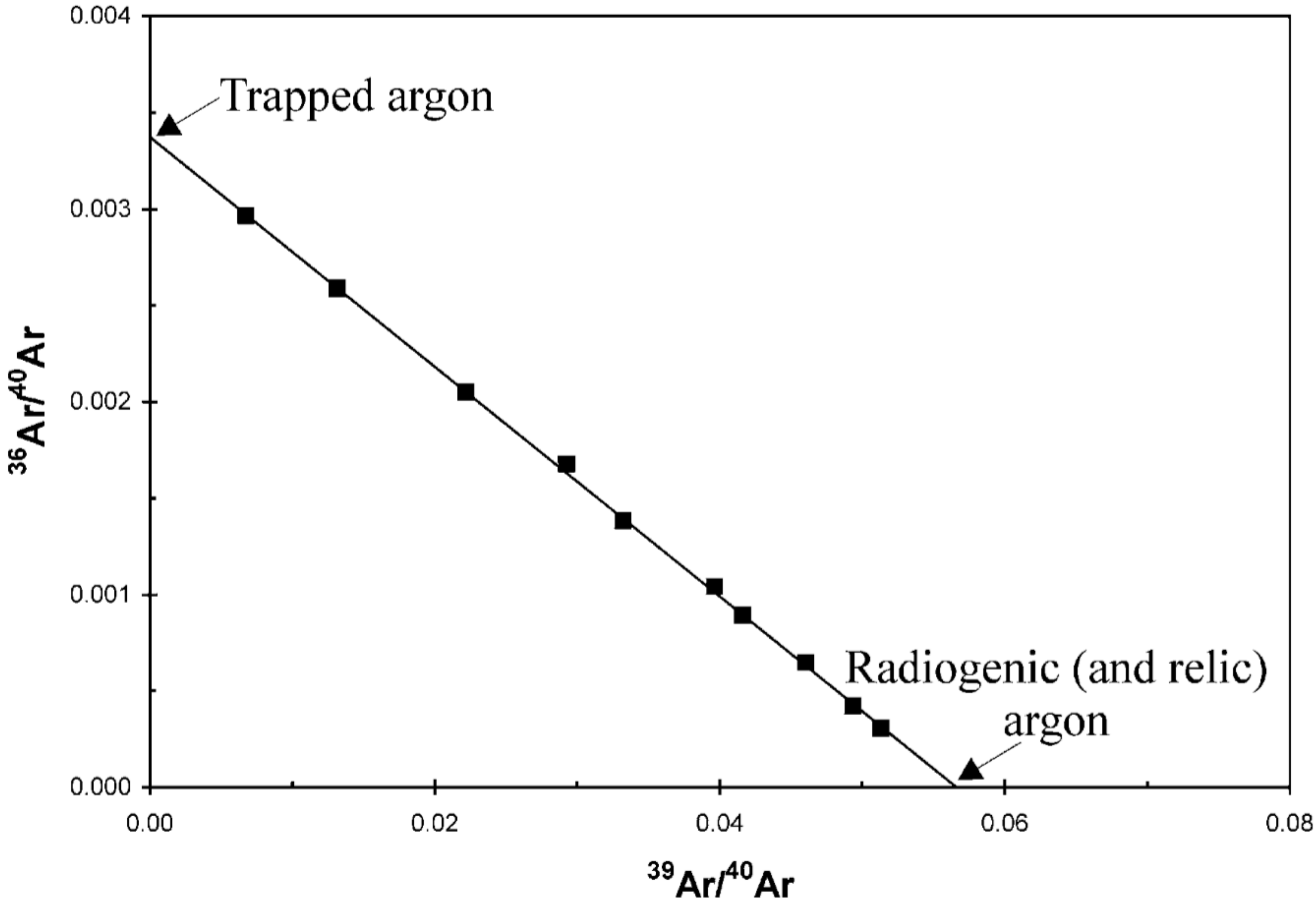


Assess Ar isotopic composition at each T step

Trapped $^{36}Ar/^{40}Ar$ value at y intercept

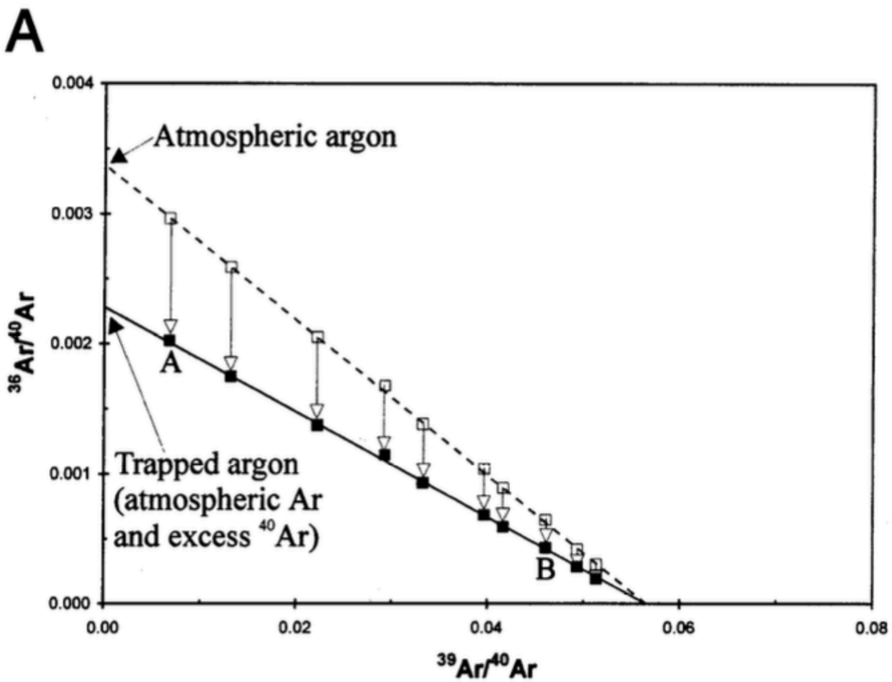
$^{39}Ar/^{40}Ar$ on x intercept

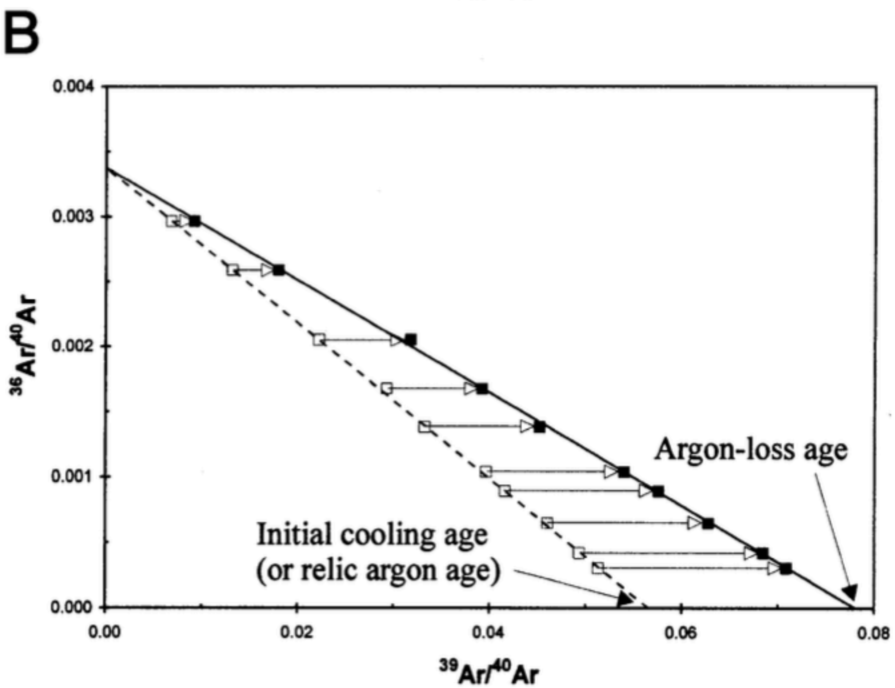
Image: https://geoinfo.nmt.edu/labs/argon/data/home.html



0.004
0.003
0.002
0.001
0.000
0.00
0.02
0.04
0.06
0.08
Trapped argon
Radiogenic (and relic) argon
$^{36}Ar/^{40}Ar$
$^{39}Ar/^{40}Ar$

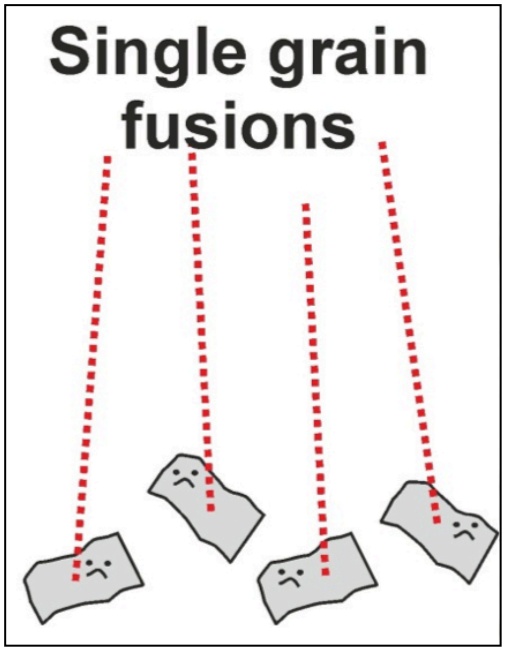
Kuiper, 2002

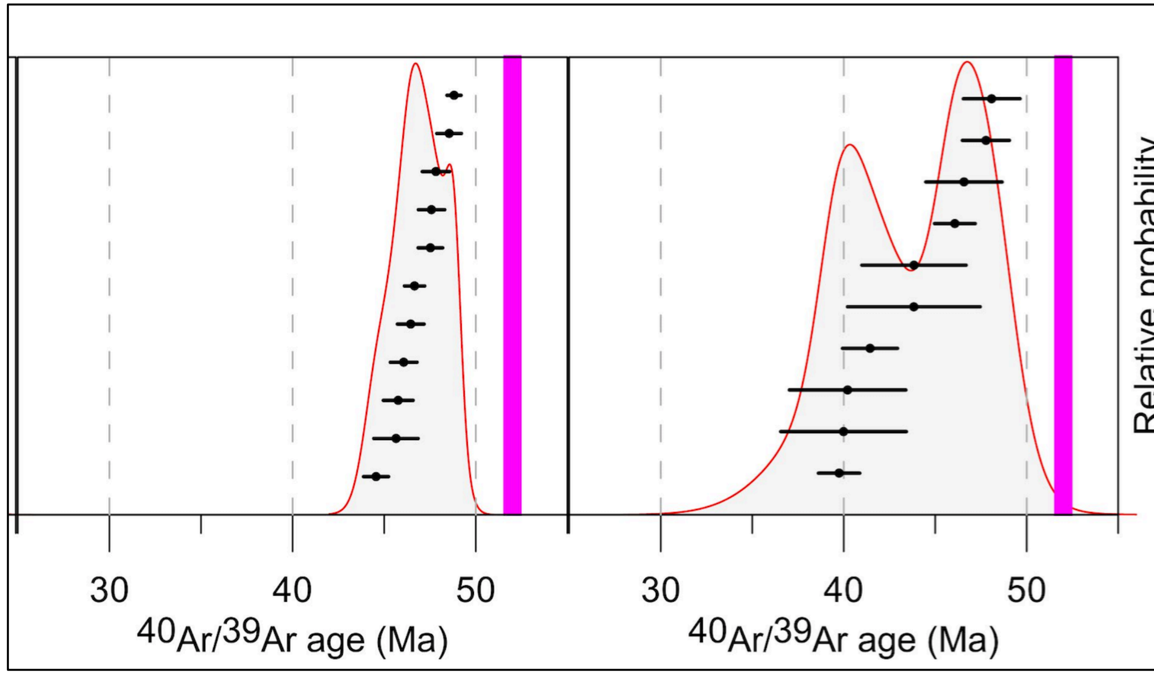

A
0.004
0.003
0.002
0.001
0.000
0.00
0.02
0.04
0.06
0.08
Atmospheric argon
A
B
Trapped argon
(atmospheric Ar
and excess ^{40}Ar)
^{36}Ar/^{40}Ar
^{39}Ar/^{40}Ar


B
0.004
0.003
0.002
0.001
0.000
0.00
0.02
0.04
0.06
0.08
Argon-loss age
Initial cooling age
(or relic argon age)
^{36}Ar/^{40}Ar
^{39}Ar/^{40}Ar

Kuiper, 2002

Dating – single grain fusion

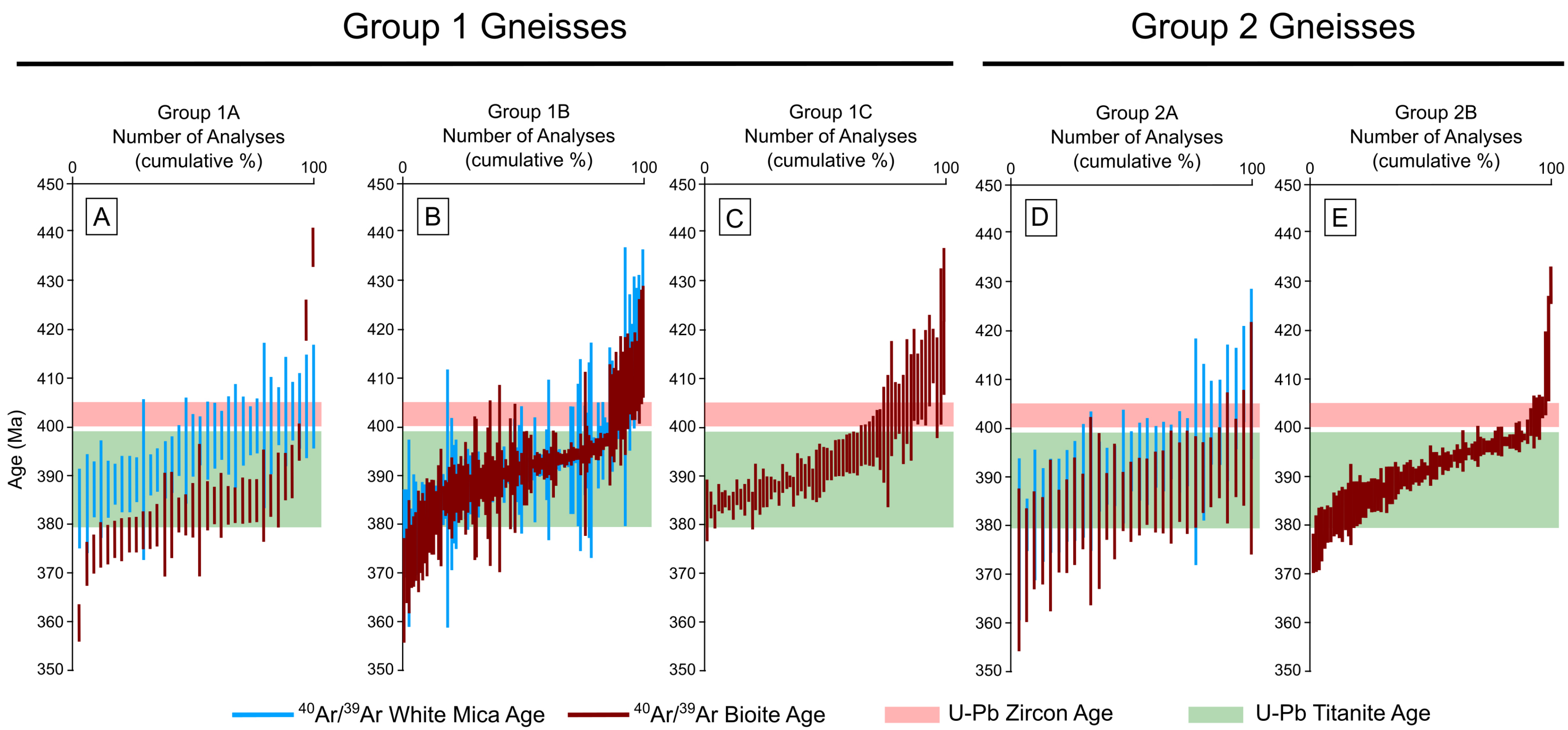




Single grain

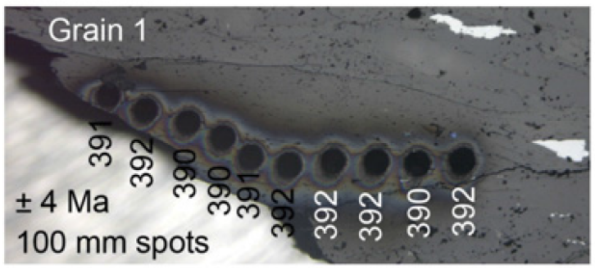
Images: Catherine Mottram; Bertram Uunk

Plotting data: single grain fusions



Dating – laser ablation

Laser probe



Single spot

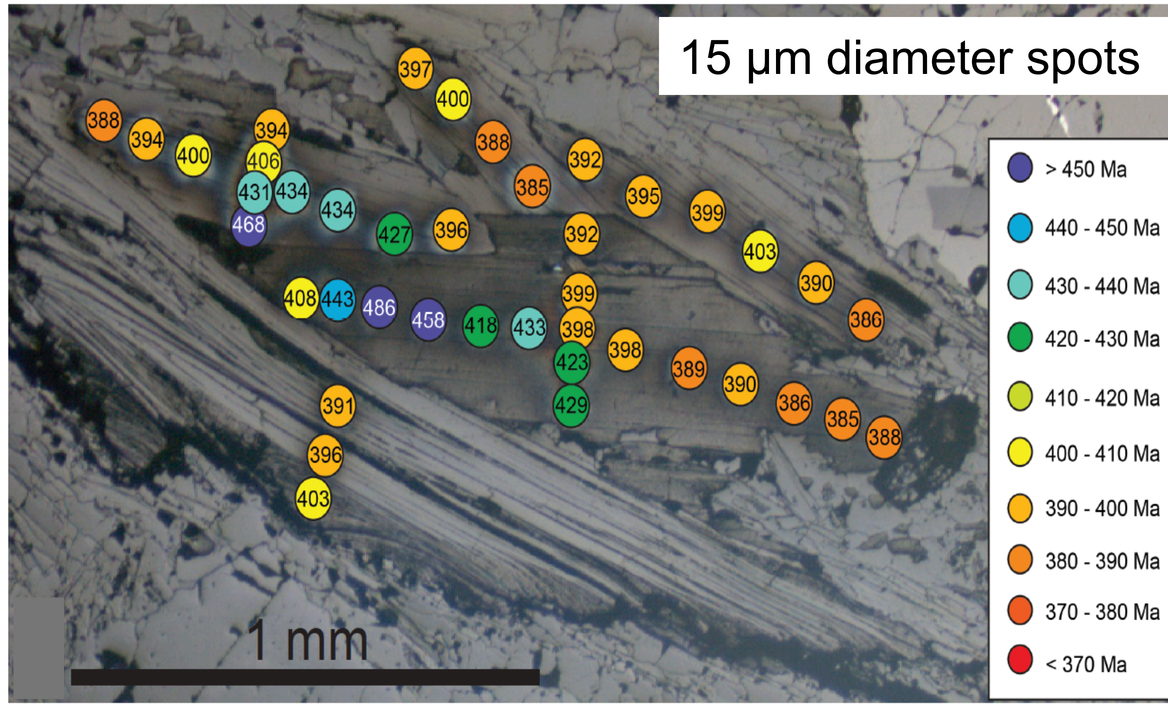


Image: Chris McDonald; McDonald et al., 2016

Minerals commonly dated with $^{40}Ar/^{39}Ar$

Formula	Mineral
$KAl_3Si_3O_{10}(OH)_2$	
$K(Mg,Fe)_3AlSi_3O_{10}(F,OH)_2$	
$(K,Na)_{0-1}(Ca,Na,Fe,Mg)_2(Mg,Fe,Al)_5(Al,Si)_8O_{22}(OH)_2$	
$KAlSi_3O_8$	
$(K,Na)AlSi_3O_8$- $CaAl_2Si_2O_8$	
$(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$	

activity TIME

Minerals commonly dated with $^{40}Ar/^{39}Ar$

Formula	Mineral
$KAl_3Si_3O_{10}(OH)_2$	Muscovite
$K(Mg,Fe)_3AlSi_3O_{10}(F,OH)_2$	Biotite
$(K,Na)_{0-1}(Ca,Na,Fe,Mg)_2(Mg,Fe,Al)_5(Al,Si)_8O_{22}(OH)_2$	Hornblende
$KAlSi_3O_8$	K-feldspar
$(K,Na)AlSi_3O_8$- $CaAl_2Si_2O_8$	Plagioclase
$(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$	Illite

Minerals commonly dated with $^{40}Ar/^{39}Ar$

- Basalt
- Tuff
- Rhyolite
- Meteorites

Can date whole rocks as young as 1000 yrs (but difficult!)

“Types” of Argon

- Atmospheric argon ($Ar_{atm)}$: $^{40}Ar/^{36}Ar = 298.56$
- Radiogenic ^{40}Ar ($^{40}Ar^*$): from natural ^{40}K decay
- Inherited/excess Ar (mixture of Ar_{atm} and $^{40}Ar^*$)
- Irradiation-induced argon (from neutron bombardment of K, Ca, Cl

Calculating the $^{40}Ar/^{39}Ar$ ratio

- ^{40}Ar needs correcting for instrument background (blank)
- And for atmospheric ^{40}Ar:
  - $^{40}Ar^* = {}^{40}Ar_{meas} - (298.56 \times {}^{36}Ar)$

- ^{39}Ar needs correcting for ^{39}Ar produced in the reactor from Ca (minor correction, ignored here)

Time to calculate some J values

activity TIME

$$J = \frac{\exp^{(\lambda t)} - 1}{R}$$

$R = {}^{40}Ar^{*} / {}^{39}Ar$

Standard	t (Ma)	Ref	R	J?
GA 1550	99.738	Renne et al 2011	0.9361	
GA 1550	99.738	Renne et al 2011	0.6752	
FCT	29.305	Renne et al 2010	1.112	

Let's calculate some ages

activity TIME

- Correct ^{40}Ar, ^{39}Ar and ^{36}Ar for background
- Correct ^{40}Ar for atmosphere (278.56)
- Calculate $^{40}Ar^*/^{39}Ar$
- Calculate age

$$\boxed{t\ (Ma) = 1804.077 \ln (1 + JR)}$$

Where J = J value
R = $^{40}Ar^*/^{39}Ar$

Grain	^{40}Ar	^{39}Ar	^{36}Ar
1	2.80241	0.10112	0.000069
2	1.64699	0.05999	0.000029
3	4.63017	0.17070	0.000009
4	1.16425	0.04235	0.000049
5	2.54924	0.09347	0.000019
6	1.29521	0.04536	0.000039
7	2.31139	0.08456	0.000049
8	5.03872	0.18459	0.000059
9	2.32016	0.08485	0.000059
10	7.54618	0.28182	0.000039
Blank	0.002958	0.000015	0.000012

$J = 0.008733$

Plot the results…

- As a plot of increasing age (*y*) vs sample (add error bars; errors given in spreadsheet)
- As an inverse isochron plot (36/40 on *y* vs 39/40 on *x*).

Discussion: sources of error

Discussion: sources of error

activity
TIME

- Age of standard
- Decay constants
- Irradiation product corrections
- J value
- Measurement uncertainties (blanks and measurements)

Learning Outcomes

- You will have an understanding of:
  - K-Ar decay
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- You will be able to:
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Extra references

- http://studylib.net/doc/18050406/ar-ar-geo--thermochronology