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 ± 0.0006 %
- ^{38}Ar = 0.0632 ± 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 x 10^9 a
  - ^{40}Ca (β decay, 89.5%)
  - ^{40}Ar (electron capture, 10.5%)

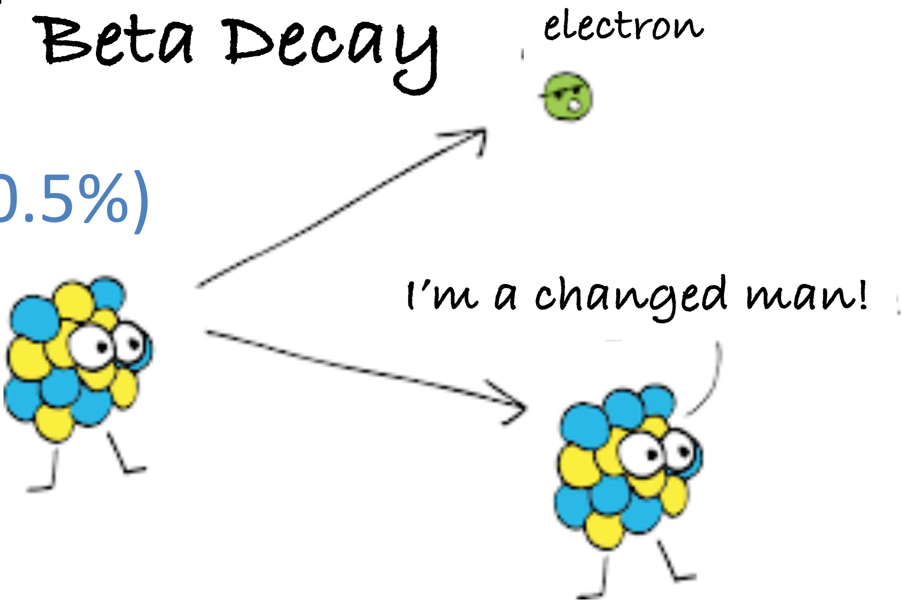


Image: Khan academy

- 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

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

Let's rearrange for t

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

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

→ 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

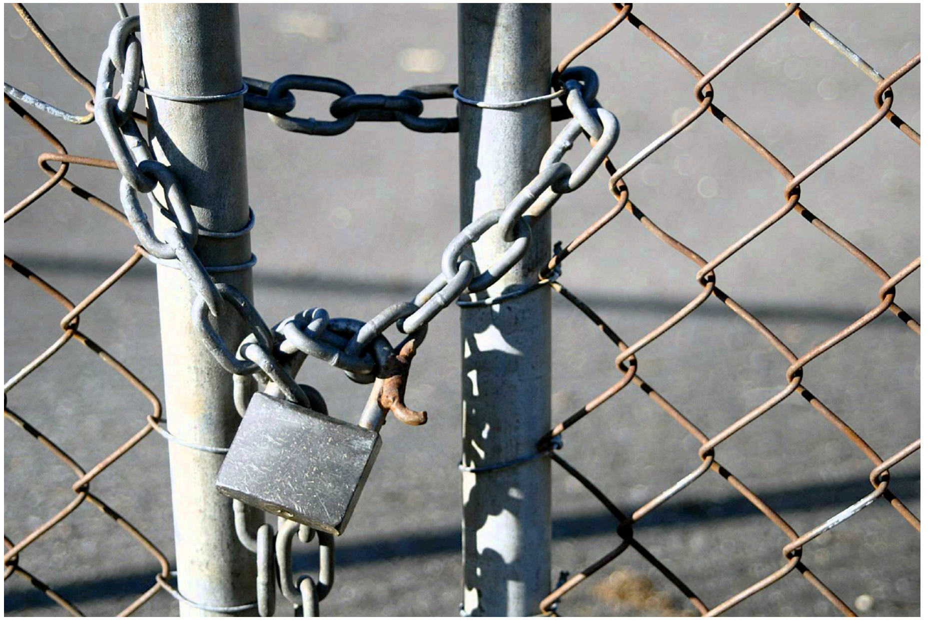
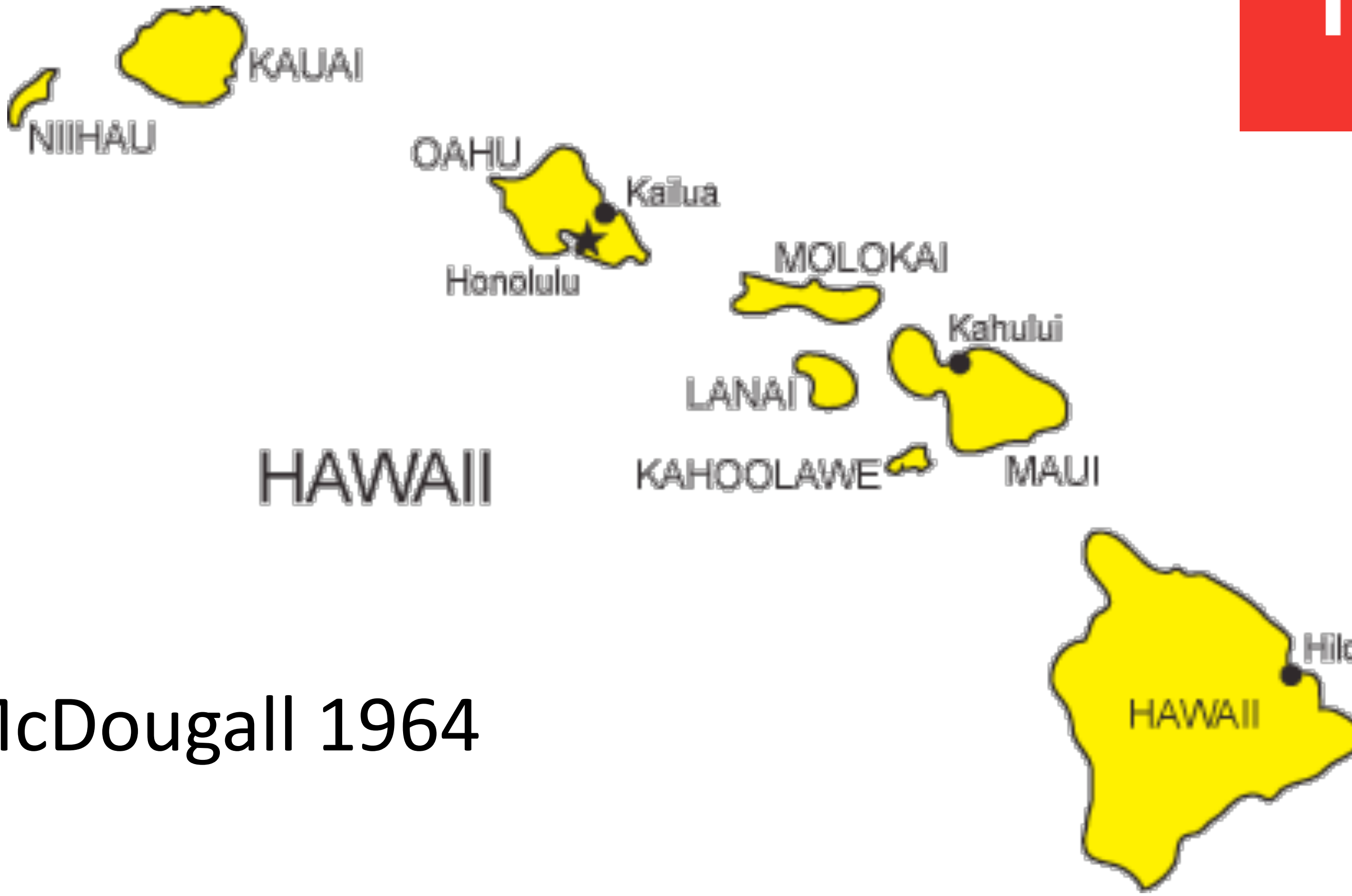


Image: YouTube.com

So let's calculate!

activity TIME



McDougall 1964

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

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	1.50×10^{-4}	1.30×10^{-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}	--	

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

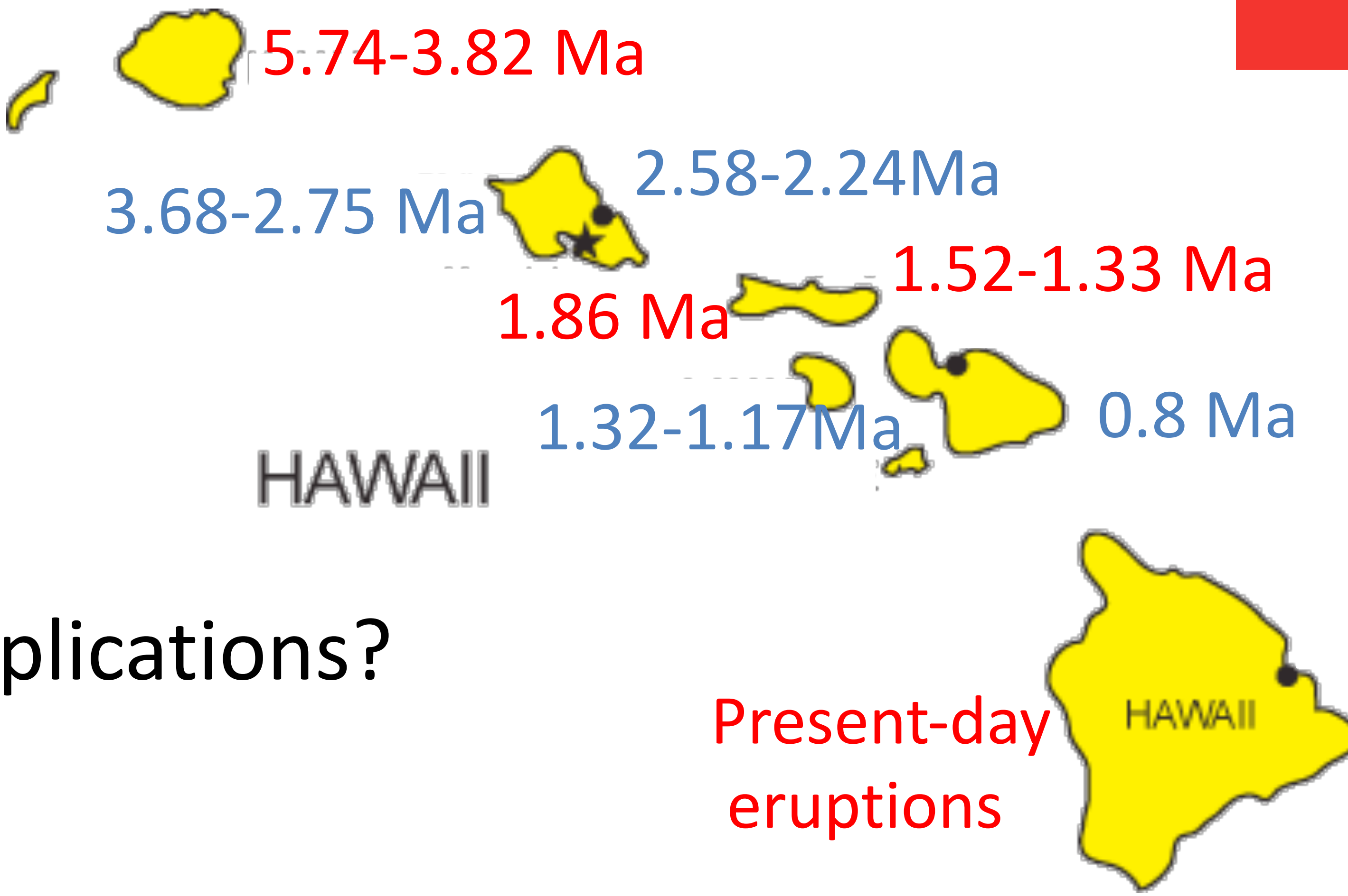
What have you found?

activity TIME

Image: state-maps.org

What have you found?

activity TIME



Implications?

Image: state-maps.org

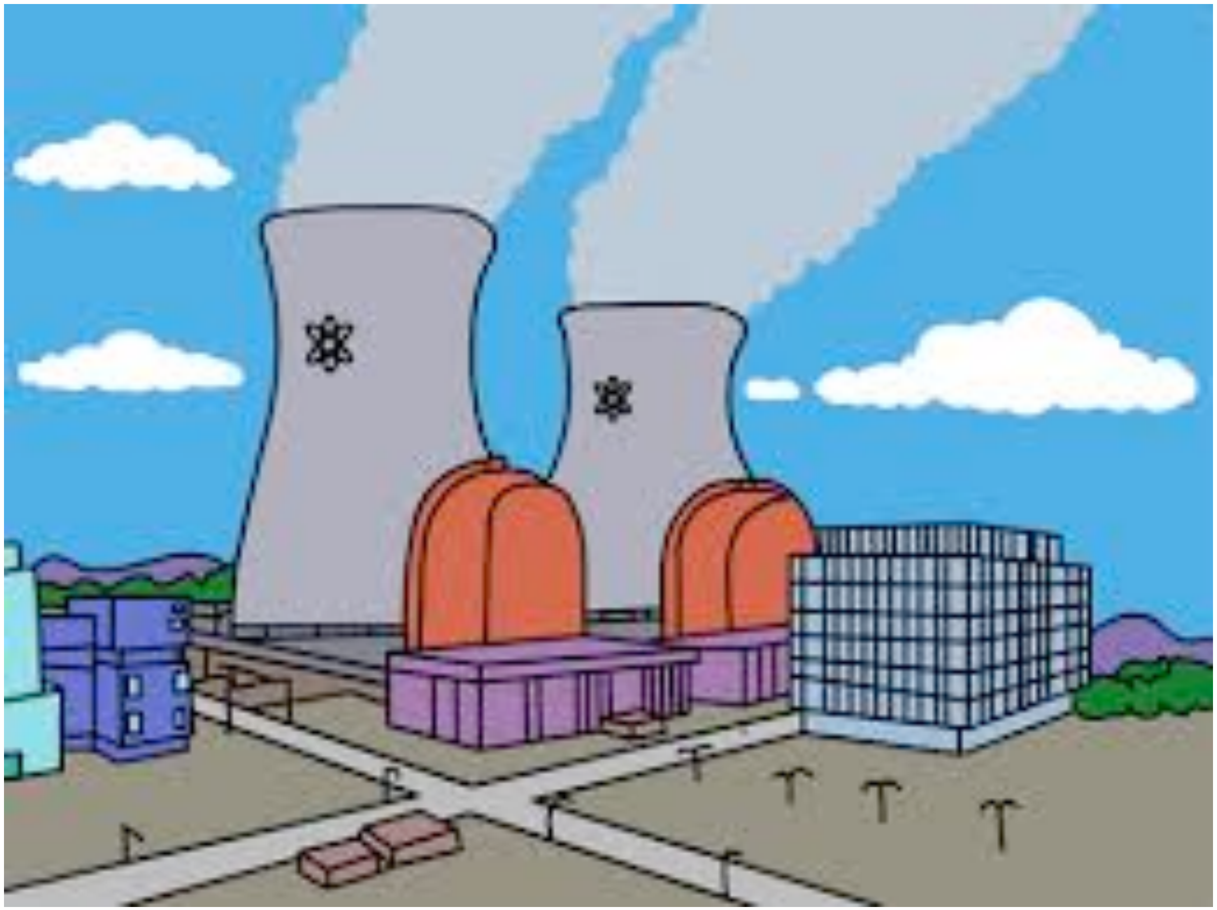
McDougall 1964

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?

activity TIME

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?
  - 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

Biotite: GA 1550; ~79 Ma

Hornblende Hb3gr; ~1074 Ma

Image: e-rocks.com

Fish Canyon Sanidine, ~28 Ma

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) = $\frac{{}^{40}Ar_{(atm\ corr)}}{{}^{39}Ar}$

And t = age of standard (Ma)

How do we date a rock or mineral?

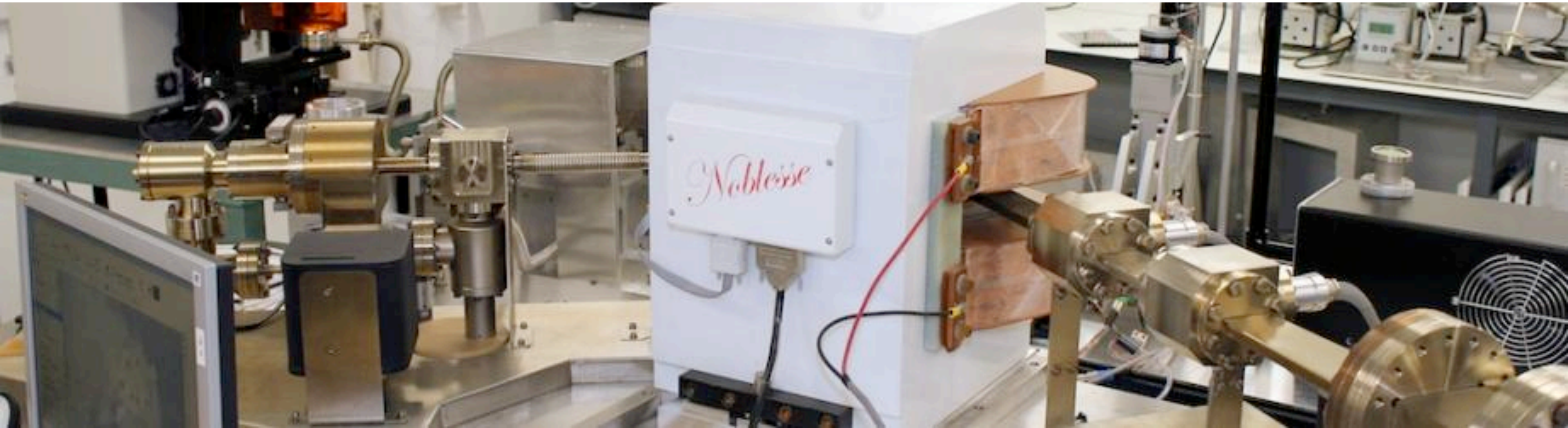
- Pick rock fragments or minerals
- Load with standards
- Irradiate
- Load into mass spec
- Heat/melt/ablate
- Measure ^{36}Ar, ^{37}Ar, ^{38}Ar, ^{39}Ar, ^{40}Ar
- Calculate J value for each sample
- Calculate sample age

Image: ScienceDaily.com

Collecting data

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

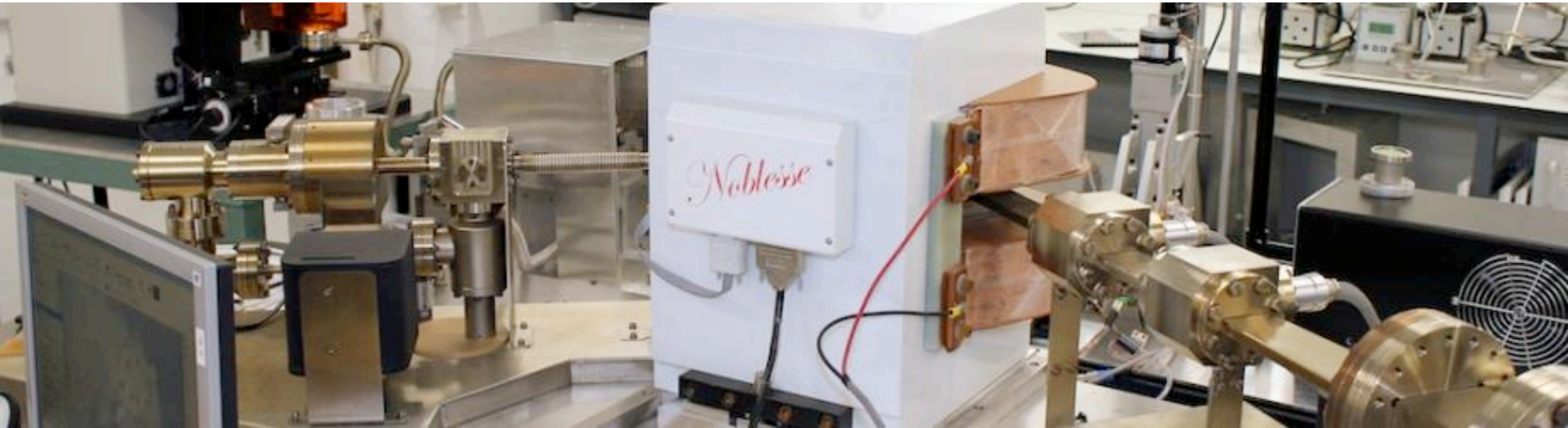
Image: Open.ac.uk



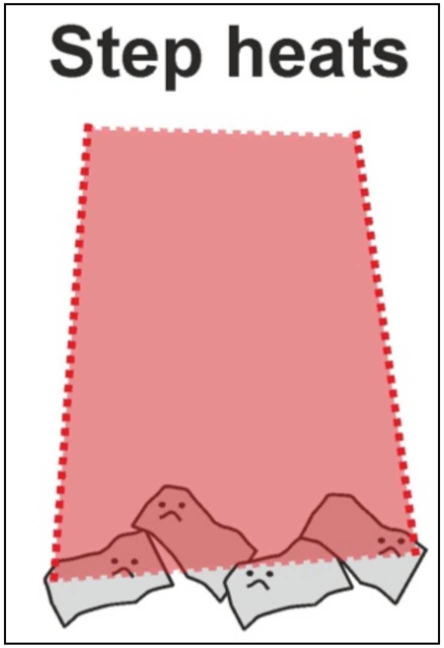
Basically

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

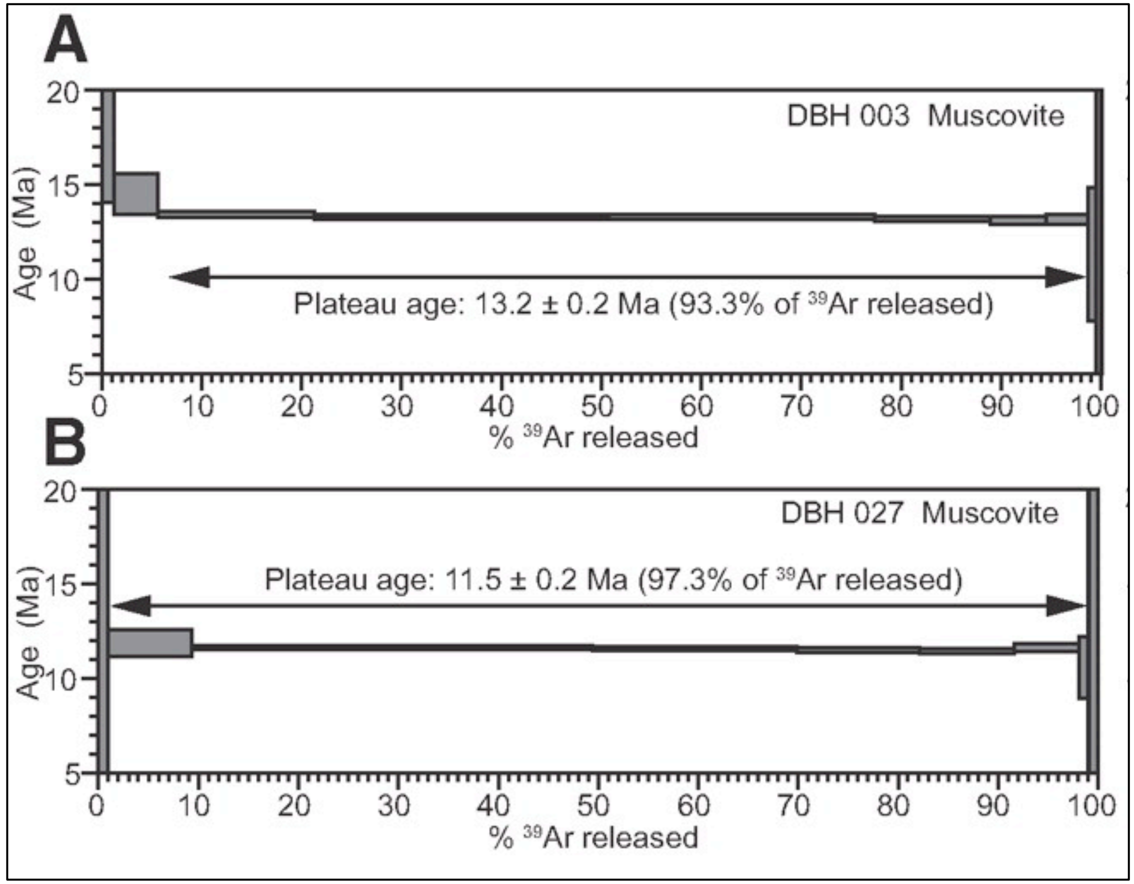
Image: Open.ac.uk



Dating – step heating



Multi-grain;
Single grain



Images: Catherine Mottram; Kellett et al., 2009

Plotting data: Step Heating

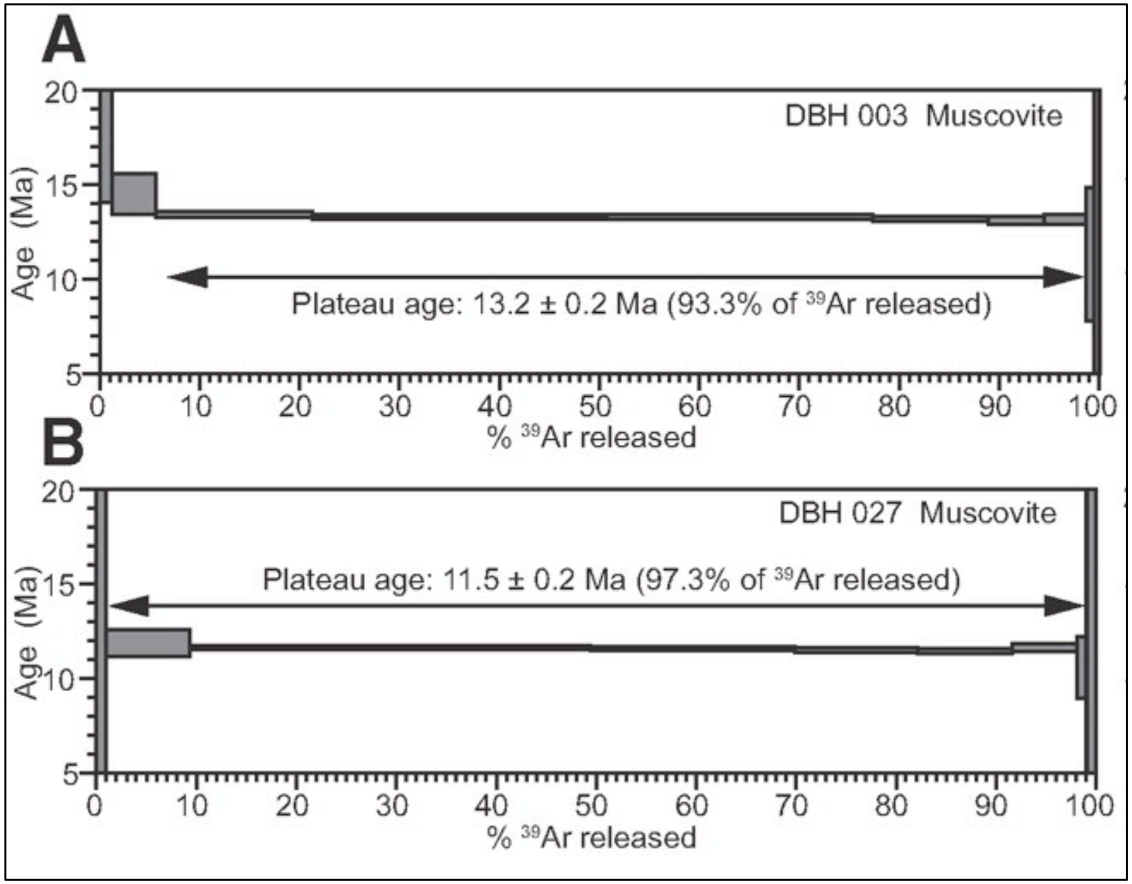


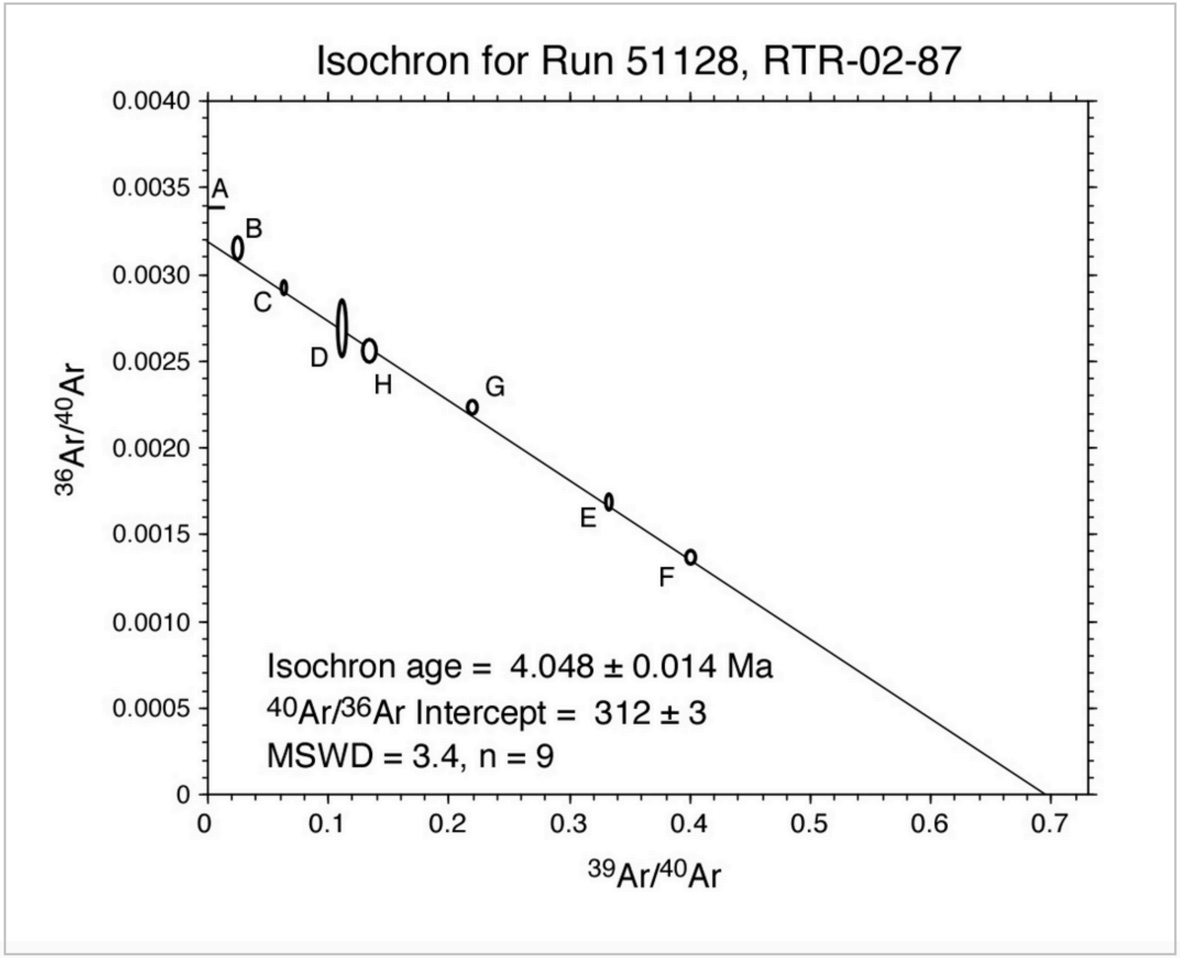
Image: Kellett et al., 2009

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

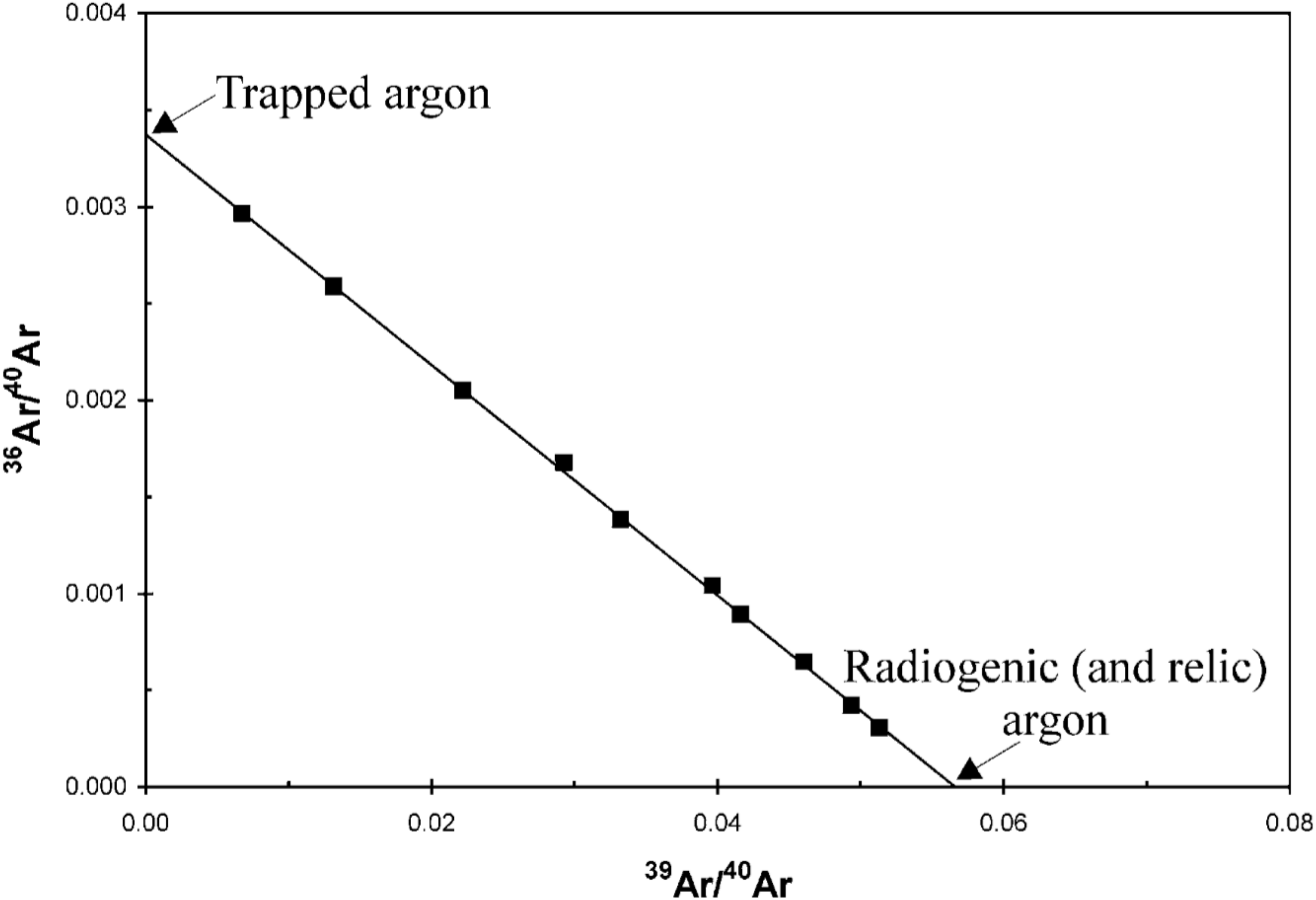


Assess Ar isotopic composition at each T step

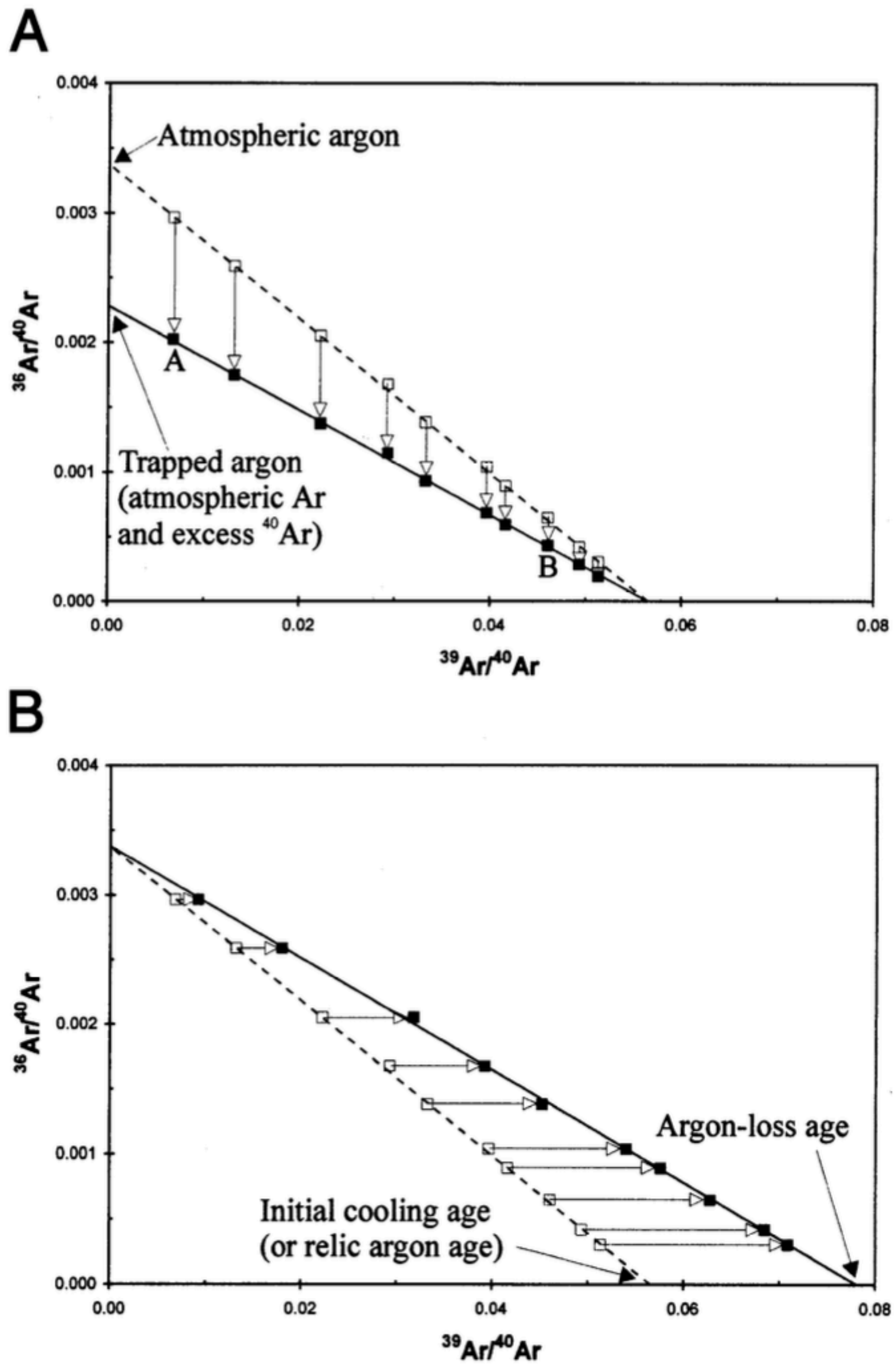
Trapped $^{36}Ar/^{40}Ar$ value at y intercept

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

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

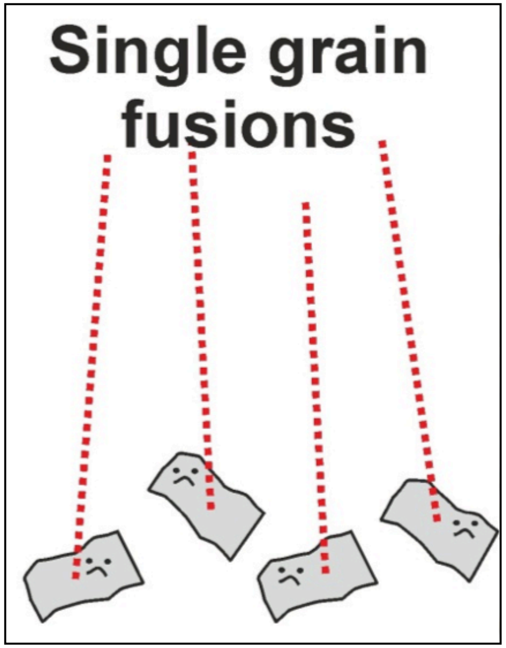

Trapped argon
Radiogenic (and relic) argon
0.004
0.003
0.002
0.001
0.000
0.00
0.02
0.04
0.06
0.08
$^{36}Ar/^{40}Ar$
$^{39}Ar/^{40}Ar$

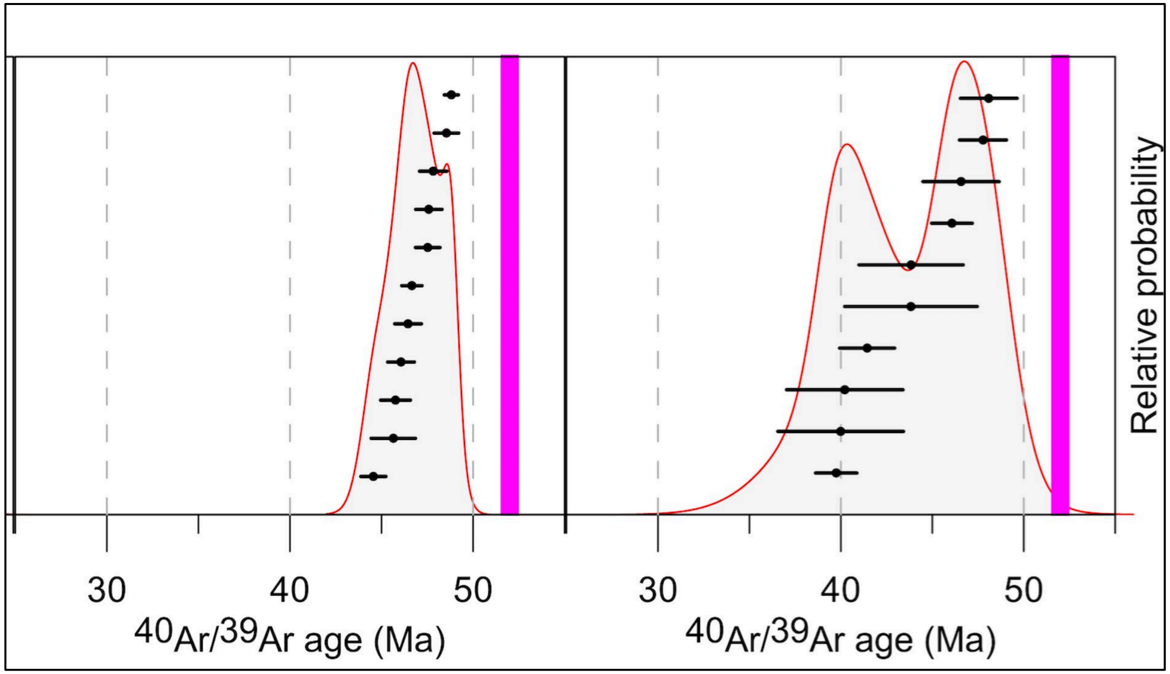
Kuiper, 2002


A
Atmospheric argon
Trapped argon
(atmospheric Ar
and excess 40Ar)
A
B
36Ar/40Ar
39Ar/40Ar
B
Initial cooling age
(or relic argon age)
Argon-loss age
36Ar/40Ar
39Ar/40Ar

Kuiper, 2002

Dating – single grain fusion





Single grain

Images: Catherine Mottram; Bertram Uunk

Plotting data: single grain fusions

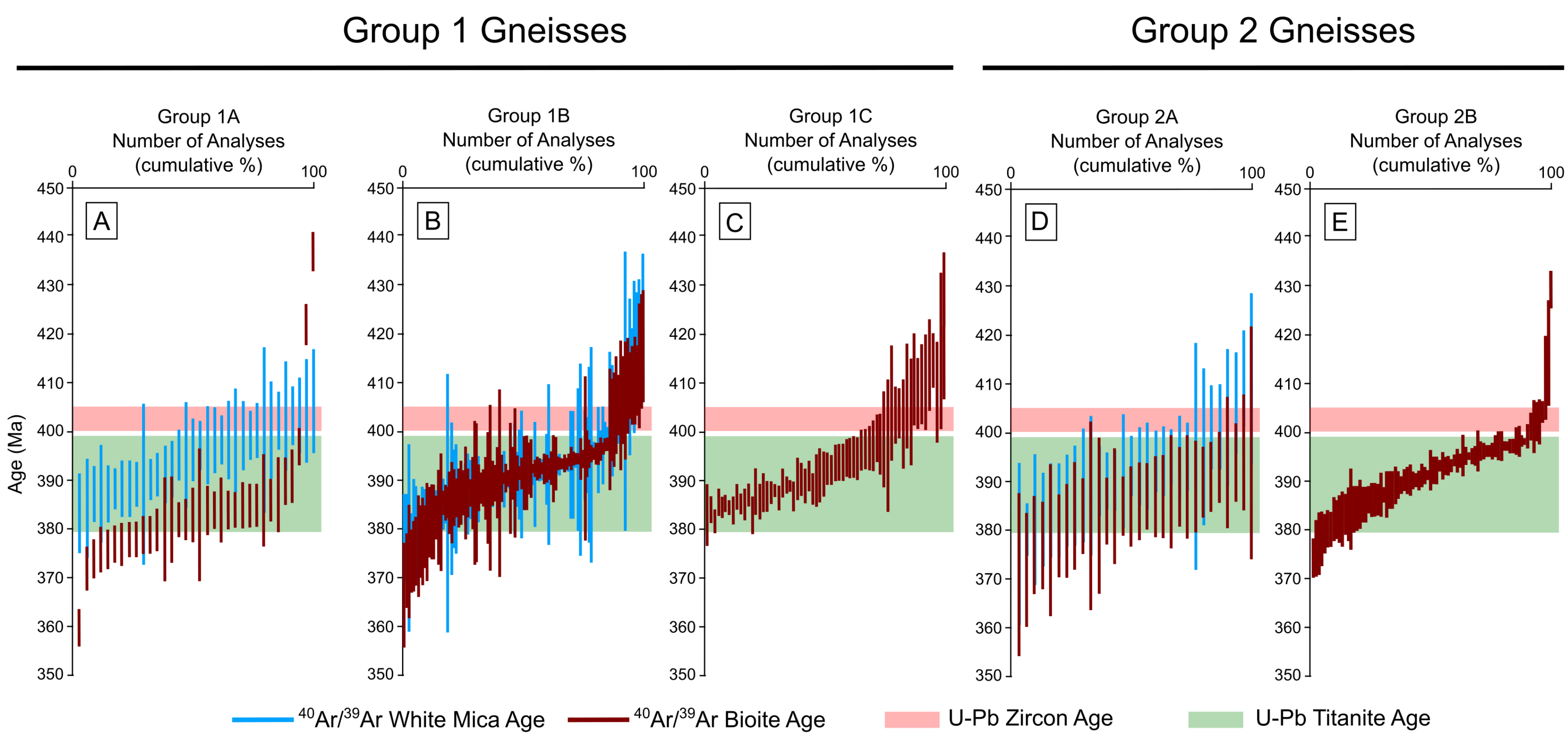
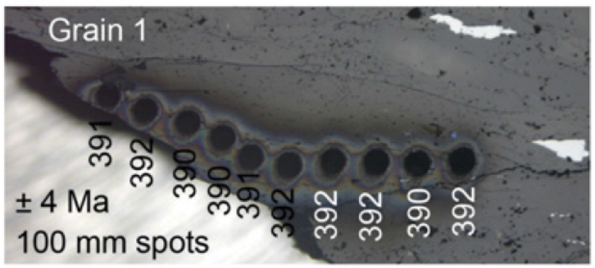


Image: McDonald et al., 2016

Dating – laser ablation

Laser probe



Single spot

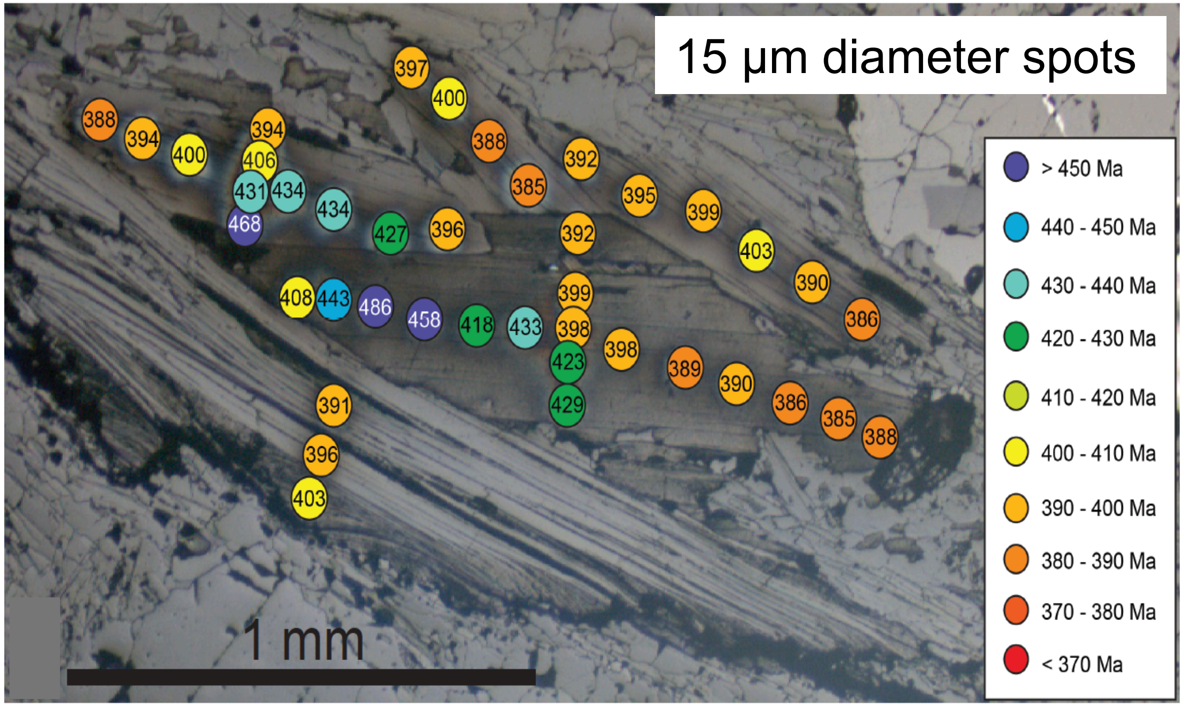


Image: Chris McDonald; McDonald et al., 2016

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

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

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	

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	97.938	Renne et al 2011	0.9361	0.06072
GA 1550	97.938	Renne et al 2011	0.6752	0.08418
FCT	29.305	Renne et al 2010	1.112	0.01472

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

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

Where J = J value

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

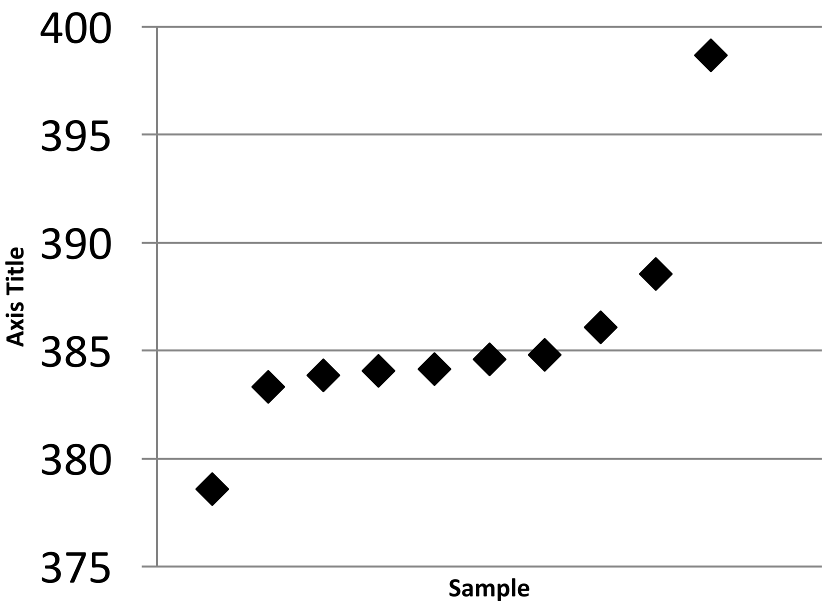
Grain	^{40}Ar	^{39}Ar	^{36}Ar
1	2.80241	0.10112	0.000069
2	1.64699	0.05999	0.000029
3	4.63017	0.17070	0.000009
4	1.16425	0.04235	0.000049
5	2.54924	0.09347	0.000019
6	1.29521	0.04536	0.000039
7	2.31139	0.08456	0.000049
8	5.03872	0.18459	0.000059
9	2.32016	0.08485	0.000059
10	7.54618	0.28182	0.000039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

J = 0.008733

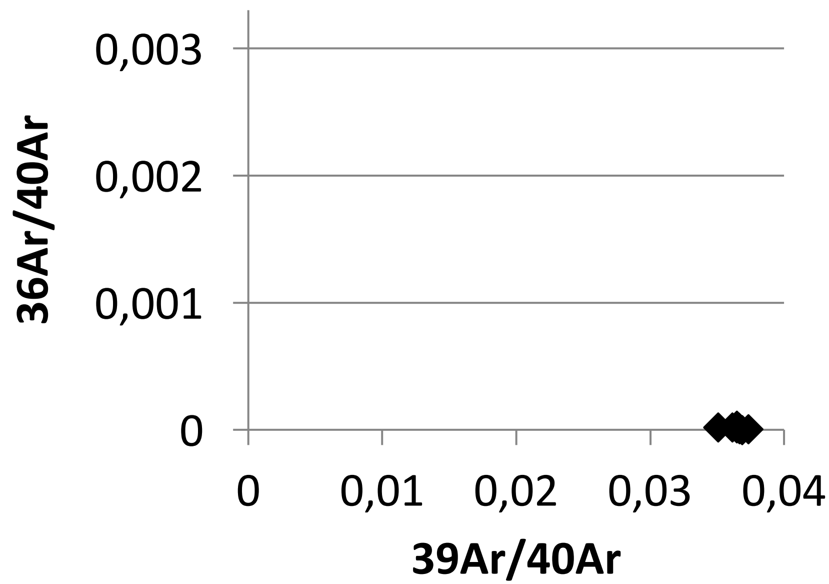
Grain	Age (Ma)
1	388.6
2	386.1
3	383.3
4	384.1
5	384.8
6	398.7
7	384.2
8	384.6
9	383.8
10	378.6

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*), with the max on *y* being the 36/40 air ratio.



Generally a coherent population with 2 outliers



Most Ar is radiogenic – little atmospheric contamination

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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  - The age equation
  - How data are collected
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- You will be able to:
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Extra references

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