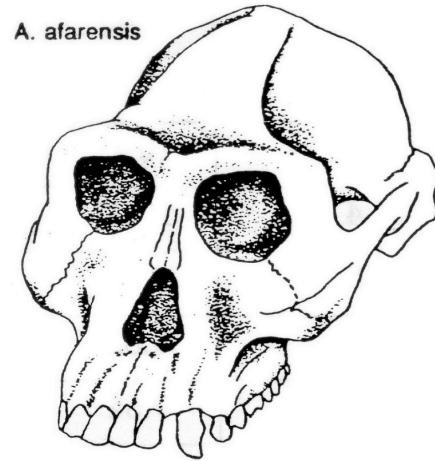# ESS 461 - ^{40}Ar/^{39}Ar dating

In today's lab, you will discover the ^{40}Ar/^{39}Ar dating method and determine an age for "Lucy" the world's most famous *Australopithecus*, who lived in the African Rift Valley in the late Pliocene.

(Not bad for a day's work ...)

A. afarensis

Recall that we derived a formula for the age of a sample in terms of the present-day abundances of a radioactive parent (N) and its daughter (D) isotope:

$$D = y\, N\left(e^{\lambda t} - 1\right)$$ ... (1)

where y is the yield of the daughter isotope and λ is the decay constant. In order to derive this from the basic radioactive decay equation, we had to make the assumption that the daughter isotope abundance in the sample was entirely due to radioactive decay of the parent. We made no allowance for the possibility that some some quantity of the daughter isotope was present when the sample formed. The presence of initial ^{40}Ar can be a major problem when dating volcanic samples with the K-Ar technique, as you will find out below.

(1) **Re-write equation (1) in a useful form for calculating ^{40}K-^{40}Ar ages.**

(2) The table on the next page gives the results of K and Ar analyses on 8 samples from individual sanidine (K-feldspar, i.e. $KAlSi_3O_8$) crystals collected from the Kada Hadar Tuff in Ethiopia. This volcanic ash deposit is an important marker bed in the Hadar Formation, from which *Australopithecus Afarensis* fossils including "Lucy" and the "First Family" were recovered in the 1970s.

K-Ar Results - Kada Hadar Tuff

Sample	wt (mg)	wt% K	^{40}Ar (10^{-13} mol)	^{36}Ar (10^{-16} mol)	$^{40}Ar/^{36}Ar$
1	9.85	11.27	7.022	3.08	2277
2	10.32	10.98	7.511	4.31	1743
3	10.41	10.77	8.415	7.59	1108
4	10.02	10.76	16.37	35.31	463.6
5	9.77	11.40	44.05	128.3	343.3
6	9.82	11.17	45.68	134.2	340.5
7	9.64	11.22	122.4	393.9	310.6
8	8.80	11.50	54.24	43.97	1233

Calculate the <u>apparent</u> K-Ar age of each sample. Are your results internally consistent? Suggest two possible explanations for the data. Can you distinguish between these possibilities using the data available?

You will need the following information:

The atomic weight of K is 39.098 g/mol, the isotopic abundance of ^{40}K is 0.01167%, the decay constant of ^{40}K is 5.5407 x 10^{-10} yr^{-1}, and the yield of ^{40}Ar from ^{40}K decay is 10.48%. The atmosphere contains 1% Ar by volume, with an isotopic ratio $^{40}Ar/^{36}Ar$ = 295.5.

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^{40}Ar-^{39}Ar dating

Both of the problems identified in Q. 2 above can be overcome (in most cases) by using a clever adaptation of the K-Ar dating technique, known as $^{40}Ar/^{39}Ar$ dating. ^{39}Ar is a short-lived isotope of Ar ($t_{1/2}$ = 269 yr) which does not occur naturally. It is made artificially <u>from ^{39}K</u> by a neutron capture reaction in a nuclear reactor:

$$^{39}K(n,p)^{39}Ar$$
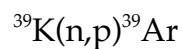
Irradiating a mineral sample converts a small amount of K into ^{39}Ar, which can be measured in the same mass-spectrometric analysis as ^{40}Ar, and the $^{40}Ar/^{39}Ar$

ratio used in place of the $^{40}Ar/^{40}K$ ratio to calculate the sample age. The yield of ^{39}Ar relative to K in the irradiation has to be determined, but rather than attempt to monitor the neutron flux and energy spectrum in the reactor, it is easier to irradiate a standard of known age at the same time as the samples, and back-calculate the ^{39}Ar yield (i.e. the standard serves as a radiation dosimeter).

The advantages of this technique are that it: (i) Eliminates errors associated with making a separate K analysis of each sample, (ii) Reduces the overall error in the dating, because isotope ratio analyses can be made much more accurately than most elemental abundance analyses, (iii) Allows gas to be extracted from single mineral grains by laser heating, enabling contaminant grains to be identified and excluded. The presence of inherited, old (xenolithic) grains in volcanic ash can seriously bias the dating of bulk samples. (iv) Allows gas to be extracted by stepwise heating at successively higher temperatures. This allows grains which have lost radiogenic daughter ^{40}Ar (by diffusion or weathering) to be identified and excluded. (v) Allows contamination by initial atmospheric Ar to be identified and corrected in the age calculation.

Sound too good to be true? Try it ...

(3) Disappointed by your previous attempts to date the Kada Hadar Ash, you send off a fraction of each of your 8 samples for irradiation, along with a sample of feldspar from the 27.8 Myr old Fish Canyon Tuff, an agreed standard for $^{40}Ar/^{39}Ar$ dating.

Mass spectrometric analysis of the irradiated samples gives the following results:

$^{40}Ar/^{39}Ar$ Results - Kada Hadar Tuff

Sample	$^{39}Ar/^{40}Ar$	$^{36}Ar/^{40}Ar$
1	7.44	4.326×10^{-4}
2	7.10	5.669×10^{-4}
3	6.27	8.957×10^{-4}
4	3.10	21.52×10^{-4}
5	1.19	29.10×10^{-4}

6	1.13	29.32 x 10^{-4}
7	0.416	32.15 x 10^{-4}
8	0.878	8.10 x 10^{-4}
Fish Cyn	0.9692	0.00

Make a ^{36}Ar/^{40}Ar (y-axis) vs ^{39}Ar/^{40}Ar (x-axis) plot of the data from the 8 Kada Hadar samples. What do you notice about the data from 7 of the 8 samples ? Can you explain this ? (Hint - what is special about the ^{36}Ar/^{40}Ar intercept of a best-fit line through the data).

Can you account for the anomalous data point ? Is the anomalous feldspar grain older or younger than the other grains ? (Hint - remember that the ^{39}Ar/^{40}Ar ratio is related to the K/Ar ratio of the sample).

Do these results explain why conventional K-Ar dating of the samples failed to give uniform age results?

(4) We can calculate the age of Kada Hadar Tuff from the 7 feldspar samples "native" to it (the one anomalous grain can be excluded from the following calculations).

When a sample is irradiated, ^{39}Ar is created according to the following complicated equation:

$$^{39}Ar = {}^{39}K \, \Delta t \int_E \phi_E \sigma_E \, dE \qquad \text{... (2)}$$

where Δt is the irradiation time and the integral describes the total number of neutrons captured to produce ^{39}Ar. Fortunately we don't have to monitor the neutron flux or solve the equation above to determine the age of a sample.

Instead, divide equation (1) by equation (2):

$$\frac{^{40}Ar}{^{39}Ar} = \frac{y \, {}^{40}K}{^{39}K} \frac{\left(e^{\lambda t} - 1\right)}{\Delta t \int \phi_E \, \sigma_E \, dE} \qquad \text{... (3)}$$

Or more simply ...

$$\frac{^{40}Ar}{^{39}Ar} = \frac{\left(e^{\lambda t} - 1\right)}{J} \qquad\qquad ... (4)$$

This equation holds for both the unknown samples and the Fish Canyon Tuff standard, because they were irradiated under the same conditions. By substituting the age and $^{40}Ar/^{39}Ar$ ratio of the standard into equation 4, we can solve for J, then feed the value of J into the same equation to get the age of our unknown.

There is one last complication before we can get the final answer! We have established from the graph in Q. 3 that the individual feldspar samples are contaminated to varying degrees with atmospheric ^{40}Ar. The ^{40}Ar in equations 3 and 4 refers strictly to the radiogenic daughter ^{40}Ar, and not to the contaminant ^{40}Ar. **How can the plot you drew in Q. 3 be used to derive the ratio of pure radiogenic ^{40}Ar to ^{39}Ar ? What is the _radiogenic $^{40}Ar/^{39}Ar$ ratio of the samples ?_ (Hint - what is the $^{36}Ar/^{40}Ar$ ratio expected in the pure radiogenic Ar component ?)**

Determine the value of J from the data for the Fish Canyon Tuff standard, assuming its age is precisely 27.8 x 10⁶ years.

Apply this value of J to calculate the age of the Kada Hadar Tuff.

How old is Lucy ?