ESS 312 Geochemistry
Simulating Earth degassing using radionuclides

CHEMICAL AND ISOTOPIC EVOLUTION OF A TWO-RESERVOIR SYSTEM

In lectures we discussed radioactive decay and build-up of a daughter isotope in a closed system. Complete “closed-system” retention of parent and daughter isotopes is critical for obtaining accurate ages in geochronology.

In contrast, let’s simulate a system of two *reservoirs*, in which the radioactive element and its daughter are transported from one reservoir to another through time. To keep things interesting, we’ll consider the case where the parent and daughter are transported at different rates, as we'd expect for two geochemically distinct elements. This is a more complex problem than the closed system, because the change in isotopic composition of the daughter element depends not only on radioactive decay of its parent, but on how the parent-daughter ratio changes as material flows from one reservoir to the other. We’ll need to keep track of the parent isotope, the daughter isotope and a stable isotope of the daughter element, in both reservoirs.

We'll work with the decay of the radioactive potassium isotope ^{40}K, to ^{40}Ar.

As you already know, K is a large-ion lithophile element. It is incompatible in all mantle minerals. Hence K has been concentrated in the crust over time.

Argon, a noble gas, is even more incompatible than K. The same processes responsible for transporting K to the crust have released Ar to the atmosphere. Ar has two stable isotopes (^{36}Ar and ^{38}Ar), in addition to ^{40}Ar, the radiogenic daughter product of ^{40}K. The initial abundance of ^{40}Ar in the early Earth was negligibly small, so almost all of the ^{40}Ar now in existence has grown since the Earth formed, half of it in the last 2-3 Gyr (the half-life of ^{40}K is 1.26 billion years). Differentiation and mantle melting early in Earth history would have transferred ^{36}Ar and ^{38}Ar into the early atmosphere, but can't have transferred ^{40}Ar.

With this in mind, we can see that a simple model of K and Ar transport could help us understand the outgassing history of the Earth. We'll model changes in the ratio of $^{40}Ar/^{36}Ar$ in the mantle and atmosphere, and find the transport and differentiation history that best fits the Earth's present-day ratios. Note – it is easier to measure the isotopic ratio of a reservoir than to measure its actual Ar isotope concentration. All available samples from the mantle, such as basalt lavas, are likely to have become enriched in Ar during melting, and may have lost volatile elements such as Ar during magma ascent, crystallisation and degassing. These processes change Ar concentrations, but have no effect on Ar isotopic ratios. We will discover that the $^{40}Ar/^{36}Ar$ ratios of the mantle and atmosphere constrain the degassing history of the Earth and help determine how much of its total K has been concentrated in the crust.

K – Ar transport model

Our mathematical model consists of a set of differential equations describing K and Ar isotope abundances in the mantle, crust (for transported ^{40}K) and atmosphere (for degassed ^{36}Ar and ^{40}Ar). Before we get to these, we need to think about the initial K and Ar abundances (in applied math these would be called *boundary conditions*, or *initial conditions*).

The abundance of ^{40}K

^{40}K is a minor isotope of K. At present, its relative abundance (in atom %) is 0.01167 % (i.e. it constitutes 0.0001167 of the atoms in a sample of natural K). The atomic weight of natural K is 39.098 g/mol.

We estimate that the silicate portion of the Earth (the crust plus mantle) has a total mass of 4.03 x 10^{27} g and has a K content of 200 parts per million by weight (i.e. 200 x 10^{-6} grams K per gram of silicate Earth). We assume that there is no K in the core. Putting these numbers together, we calculate that the present-day Earth contains 1.45 x 10^{42} atom of ^{40}K:

$$4.03 \text{ x } 10^{27} \text{ x } 200 \text{ x } 10^{-6} \text{ x } 6.022 \text{ x } 10^{23} \text{ x } 0.0001167 / 39.098 = 1.45 \text{ x } 10^{22} \text{ atom } ^{40}K$$

To calculate the initial abundance, we re-arrange the radioactive decay equation:

$$^{40}K_0 = {}^{40}K \times e^{\lambda t} = 1.45 \times 10^{42} \times e^{(5.5407 \times 10^{-10} \times 4.5 \times 10^{9})} = 1.75 \times 10^{43}$$

giving an initial ^{40}K abundance of 1.75 x 10^{43} atoms.

Initial Ar abundances

We will assume that the Earth began life with 4 x 10^{39} atoms of ^{36}Ar, initially entirely in the mantle. By the end of this exercise we will discover that this is too simple an assumption. The initial abundance of ^{40}Ar is zero in both mantle and atmosphere.

Radioactive decay of ^{40}K

Note that ^{40}K decays by two mechanisms. 89.52% of the atoms that decay produce ^{40}Ca by the beta process. The other 10.48%of the atoms decay by the combination of electron capture and positron emission, both of which convert a proton in the nucleus into a neutron, decreasing the atomic number Z by 1. To account for the fact that only 10.48% of ^{40}K decays produce ^{40}Ar, we need to add a *yield* term to the standard isotope growth equation:

$$\frac{d^{40}Ar}{dt} = -y\frac{d^{40}K}{dt} = -y\ \lambda_K\ ^{40}K \qquad (2a)$$

$$^{40}Ar = y\ ^{40}K\left(e^{\lambda t} - 1\right) \qquad (2b)\quad \text{..where } y = 0.1048$$

Element transport from the mantle to the crust and atmosphere

To simulate transport of K and Ar from the mantle to the crust and atmosphere, we will assume that each year, melting of the mantle removes a fixed fraction of the total K and Ar present in the mantle. [There is a justification of this, based on what we know about the rate of mantle melting and the separation of trace elements such as Ar into magmas, in an appendix to the lab, which you can download from the class website].

The mathematical statement of this assumption is a set of 'first-order' transport equations of the form:

$$\frac{dI_M}{dt} = -\alpha_I\ I_M \qquad (3)$$

for an element or isotope whose total abundance in the mantle is I_M. Here, α_I is the 'transport coefficient' for element I, with units of t^{-1}, representing the fraction of I transferred out of the mantle per year.

Notice how similar equation (3) is to the differential equation describing radioactive decay. Instead of a decay constant, we have a *transport coefficient* α_I which describes the fractional decrease in the amount of I per year *due to transport processes*. α_I has units of t^{-1} or 'per year', just like a radioactive decay constant.

Isotopes of a given element behave in a chemically identical way to one another, hence they have the same transport coefficient. But different elements, such as Ar and K, will have different transport rates, described by different transport coefficients. As the Earth differentiates, these elements flow from the mantle to the crust and atmosphere at different rates, changing the K-Ar ratio (the parent-daughter ratio) in the reservoirs as they do so.

We will want to find values for the K and Ar transport coefficients that yield the correct abundances of K and Ar in the present-day crust and atmosphere of our simulation, and correct Ar isotopic ratios in the mantle and atmosphere.

> Download the K-Ar lab excel template from the class web site. Set up your spreadsheet with cells for the transport coefficients α_{Ar} and α_K equal to an initial value of 10^{-10} yr^{-1}.
>
> Confirm the values in cells for each of the ^{40}K decay constant ($\lambda_K = 5.5407 \times 10^{-10}$ yr^{-1}) and the ^{40}Ar yield (y = 0.1048).
>
> The first column keeps track of time. It starts with t = 0 (formation of the Earth) and divides the subsequent history into 45 time steps of Δt = 100 Myr (10^8) years each. The next six columns keep track of:
>
> | Mantle | | | Crust + Atmosphere | | |
> |---|---|---|---|---|---|
> | $^{36}Ar_M$ | $^{40}Ar_M$ | $^{40}K_M$ | $^{36}Ar_A$ | $^{40}Ar_A$ | $^{40}K_C$ |

Transport and radioactive decay equations

We describe the changes in the amount of each isotope in each reservoir by differential equations that incorporate the effects of radioactive decay and transport. We need 6 equations to describe the complete system, but they are *interdependent.* For example, K lost from the mantle is added to the crust, K decaying in the mantle becomes ^{40}Ar, which is then distributed between the mantle and atmosphere, and so on. For simplicity, we will assume that the 'crust + atmosphere' represents a single reservoir, so that ^{40}Ar produced by K decay in the crust immediately escapes into the atmosphere.

By applying these equations to a fixed time step Δt, we change differential equations like (2a) and (3) into "difference equations", which are easier to incorporate into the spreadsheet:

DIFFERENTIAL EQUATION	DIFFERENCE EQUATION UPDATES THE SOLUTION FROM TIME **t** TO **t + Δ**t
$\frac{d}{dt}\left({}^{36}Ar_M\right) = -\alpha_{Ar}\ {}^{36}Ar_M$	$\Rightarrow\ {}^{36}Ar_{M,t+\Delta t} = {}^{36}Ar_{M,t} - \alpha_{Ar}\,\Delta t\ {}^{36}Ar_{M,t}$

$$= \left(1-\alpha_{Ar}\,\Delta t\right)\,{}^{36}Ar_{M,t} \qquad ..(4)$$

$$\frac{d}{dt}\left({}^{36}Ar_A\right) = +\alpha_{Ar}\;{}^{36}Ar_M \quad \Rightarrow \quad {}^{36}Ar_{A,t+\Delta t} = {}^{36}Ar_{A,t} + \left(\alpha_{Ar}\,\Delta t\right)\,{}^{36}Ar_{M,t} \qquad ..(5)$$

$$\frac{d}{dt}\left({}^{40}K_M\right) = -\alpha_K\;{}^{40}K_M - \lambda_K\;{}^{40}K_M \quad \Rightarrow \quad {}^{40}K_{M,t+\Delta t} = \left(1-\alpha_K\,\Delta t - \lambda_K\,\Delta t\right){}^{40}K_{M,t} \qquad ..(6)$$

$$\frac{d}{dt}\left({}^{40}K_C\right) = +\alpha_K\;{}^{40}K_M - \lambda_K\;{}^{40}K_C \quad \Rightarrow \quad {}^{40}K_{C,t+\Delta t} = \left(\alpha_K\,\Delta t\right){}^{40}K_{M,t} + (1-\lambda_K\,\Delta t)\;{}^{40}K_{C,t} \qquad ..(7)$$

$$\frac{d}{dt}\left({}^{40}Ar_M\right) = \lambda_K\;y\;{}^{40}K_M - \alpha_{Ar}\;{}^{40}Ar_M$$

$$\Rightarrow \quad {}^{40}Ar_{M,t+\Delta t} = \left(\lambda_K\;y\,\Delta t\right){}^{40}K_{M,t} + (1-\alpha_{Ar}\,\Delta t)\;{}^{40}Ar_{M,t} \qquad ..(8)$$

$$\frac{d}{dt}\left({}^{40}Ar_A\right) = \alpha_{Ar}\;{}^{40}Ar_M + \lambda_K\;y\;{}^{40}K_C$$

$$\Rightarrow \quad {}^{40}Ar_{A,t+\Delta t} = \qquad ..(9)$$

Q.1 Complete equation (9) above.

The difference equations shown above have been built into the spreadsheet. To the right of the isotope abundace columns are two graphs, showing: (i) Abundances of ^{36}Ar, ^{40}K and ^{40}Ar in the *mantle*, (ii) Isotope ratios (^{40}Ar/^{36}Ar) in the mantle and atmosphere.

How well does this model represent the real Earth? Some diagnostic data:

Above the graphs is a block of cells showing results of the model ("model output") and some real geochemical data for comparison. Use the values in these cells K3 to L11 to help you understand the effects of changing the K and Ar transport coefficients:

In cells K3 to K11 are model predictions for:

(K3) The fraction of the Earth's K transferred to the crust by the end of the simulation. *Careful* – dividing the final value for crustal ^{40}K (line 59) by the initial value in the mantle (line 14) gives far too low a value, because it includes the radioactive decay of ^{40}K. We want to know about the chemical transport of the (far more abundant) non-radioactive K isotopes. So this is calculated from the ratio $^{40}K_{crust,final}$ / ($^{40}K_{mantle,final}$ + $^{40}K_{crust,final}$).

(K4) The final concentration of K in the crust. (Calculated assuming the mass of the crust is 2.6×10^{25} g, and using the present-day ratio of ^{40}K/total K = 0.0001167. The continental crust contains roughly 1% K by weight.

(K5) The fraction of the Earth's total ^{36}Ar outgassed to the atmosphere by the end of the run. (Final atmospheric ^{36}Ar (G59) divided by the total ^{36}Ar (G59+C59)).

(K6) The atmospheric ^{40}Ar abundance (in moles) at the end of the run. The actual abundance is 1.65×10^{18} moles.

(K7) The fraction of the total ^{40}Ar in the atmosphere at the end of the run.

(K8) The $^{40}Ar/^{36}Ar$ ratio of the mantle at the end of the run. The value measured in mid-ocean ridge basalts is > 1000.

(K9) The $^{40}Ar/^{36}Ar$ ratio of the atmosphere at the end of the run. This value in the present day atmosphere is 295.5.

(K10) The $^{40}K/^{36}Ar$ ratio of the mantle at the end of the run.

(K11) The ratio $^{40}K_{crust}/^{36}Ar_{atm}$ at the end of the run.

This value, along with the $^{40}K/^{36}Ar$ ratio of the mantle, will help you understand how the isotope ratios evolve in the atmosphere and mantle.

Effect of transport on K and Ar concentrations in the mantle and crust + atmosphere

Start by setting the transport coefficients α_{Ar} and α_K to zero (you'll get a lot of 'divide by zero' errors, but don't worry about these). In this case, nothing is transported and no crust or atmosphere forms.

Q.2 Describe and explain the shape of the curves in the top graph, which show ^{36}Ar, ^{40}K and ^{40}Ar abundances in the mantle.

^{36}Ar:

^{40}K:

^{40}Ar:

Q.3 When no transport occurs, what is the final ^{40}Ar/^{36}Ar ratio in the mantle?

Now reset both transport coefficients to 1.0×10^{-10} yr^{-1}. You should see non-zero values for $^{40}K_C$, $^{36}Ar_A$ and $^{40}Ar_A$ re-appear in the spreadsheet.

To study the effect of changing the *rate* of element transfer, change the transport co-efficients to values of:

$\alpha_K = \alpha_{Ar} = 10^{-11}$,

$\alpha_K = \alpha_{Ar} = 10^{-10}$,

$\alpha_K = \alpha_{Ar} = 5 \times 10^{-10}$

In these initial cases, be sure to assign both elements *the same* transport coefficient.

Q.4 Complete the following table:

	$\alpha_K = \alpha_{Ar} = 10^{-11}$	$\alpha_K = \alpha_{Ar} = 10^{-10}$	$\alpha_K = \alpha_{Ar} = 5 \times 10^{-10}$
% ^{36}Ar degassed			
$^{40}Ar/^{36}Ar_{mantle}$			
$^{40}Ar/^{36}Ar_{atmosphere}$			

Q.5 Describe how the curves showing $^{36}Ar_{mantle}$, $^{40}K_{mantle}$ and $^{40}Ar_{mantle}$ change as the rate of transport / degassing increases.

Q.6 Optional – bonus question – can you derive a simple equation that predicts the % ^{36}Ar degassed from the mantle? Hint – notice the similarity between the $^{36}Ar_m$ curve in your graphs and graphs you've worked with describing decay of a radioactive parent isotope ...

Q.7 Neglecting small (~1%) differences which result from the coarse method we're using to solve these differential equations, what do you notice about the final $^{40}Ar/^{36}Ar$ ratios in the mantle and atmosphere in all of the simulations you've run so far? Explain this.

Hint – you may want to go back and look at the final $^{40}K/^{36}Ar$ ratios in the mantle and the (crust + atmosphere) for the various transport coefficients.

Fractionation of K from Ar due to transport.

Although both K and Ar are expected to behave as incompatible elements, we do not expect them to have identical behavior. i.e. We expect that magmatic processes involved in differentiation will separate these elements, resulting in *different K/Ar ratios* in the two reservoirs in our model. Let's simulate this, and see what effect differential transport has on the *isotopic evolution* of the mantle and atmosphere.

Start by making Ar more incompatible than K (this is the actual behavior)

Set $\alpha_K = 1 \times 10^{-10}\ yr^{-1}$

Set $\alpha_{Ar} = 5 \times 10^{-10}\ yr^{-1}$

i.e. The fraction of Ar removed from the mantle every time-step will be 5 x greater than the fraction of K. Note that this affects both isotopes of Ar, *but it cannot have much effect on ^{40}Ar initially, because this isotope must first be produced by ^{40}K decay*.

Q.8 What effect does this have on the final $^{40}Ar/^{36}Ar_{mantle}$ and $^{40}Ar/^{36}Ar_{atmosphere}$ ratios?

Are they the same?

How do they compare to the ratios you entered in the table above for Q.4?

Now (hypothetically), reverse the values of the transport coefficients, to simulate the hypothetical case in which K is more incompatible than Ar:

Set $\alpha_K = 5 \times 10^{-10}$ yr^{-1}

Set $\alpha_{Ar} = 1 \times 10^{-10}$ yr^{-1}

Q.9 Describe the effect this has on the final $^{40}Ar/^{36}Ar_{mantle}$ and $^{40}Ar/^{36}Ar_{atmosphere}$ ratios, and explain this behavior.

Before proceding, be sure that you understand that the isotopic ratios ($^{40}Ar/^{36}Ar$) that grow in to the mantle and atmosphere depend on the K/Ar ratios in each reservoir. If $^{40}K/^{36}Ar$ in the mantle is high, it will acquire a high $^{40}Ar/^{36}Ar$ ratio through time, and *vice versa*.

Simulating Earth evolution: Separation of K and Ar during differentiation of the mantle, crust and atmosphere:

We believe the average K content of the crust is 1% by weight. Experiment with varying the K transport coefficient (α_K) to obtain a K concentration close to 1% in the crust at the end of the simulation.

Q.10 What value of α_K gives a final K concentration in the crust of 1%?

Leave this value of α_K fixed from now on.

Ar isotopic ratios in the mantle and atmosphere:

We now have two more observed quantities we can try to match, the total ^{40}Ar content of the atmosphere, and the $^{40}Ar/^{36}Ar$ ratio in the Earth's atmosphere. Start by adjusting the value of α_{Ar} so as to match the total ^{40}Ar content of the Earth's atmosphere:

Q.11 What value of α_{Ar} results in a final atmospheric ^{40}Ar content of 1.65×10^{18} moles?

Q.12 For this choice of of α_{Ar} , what are the final values for the ratios: **$^{40}Ar/^{36}Ar_{mantle}$** **$^{40}Ar/^{36}Ar_{atmosphere}$** **Do these match the actual values?**

You should find that matching the ^{40}Ar content of the atmosphere results in mantle and atmospheric $^{40}Ar/^{36}Ar$ ratios that are too low, and too high, respectively. As further confirmation, now increase the value of α_{Ar} until you reach a mantle $^{40}Ar/^{36}Ar$ ratio that is > 1000.

Q.13 What value of α_{Ar} is required to give a final mantle $^{40}Ar/^{36}Ar$ ratio > 1000?

Q.14 For this value of α_{Ar}, what is the predicted amount of ^{40}Ar in the atmosphere?

Does this match the actual amount of ^{40}Ar in the atmosphere?

What is the predicted percentage outgassing of ^{36}Ar from the mantle?

What is the predicted percentage outgassing of ^{40}Ar from the mantle?

Q.15 Nitrogen as N_2 behaves similarly in melting and other geochemical processes to Ar. What does the Ar model suggest about the concentration of nitrogen (and similar volatile elements) remaining in the mantle?

One last problem

To obtain a mantle $^{40}Ar/^{36}Ar$ ratio > 1000 in question 14 required a high value for α_{Ar}. You should have noticed that this produced too high an atmospheric ^{40}Ar abundance – greater than the actual value of 1.65 x 10^{18} moles (which we know precisely).

Thus we have a dilemma —the high $^{40}Ar/^{36}Ar$ ratio of the mantle indicates that ^{36}Ar is thoroughly outgassed, but the ^{40}Ar abundance in the atmosphere suggests ^{40}Ar is not so extensively outgassed.

How can this be? Surely both Ar isotopes must have the same transport behavior? ...

The problem can be resolved if degassing was much more rapid early in Earth history. At that time, ^{36}Ar could be degassed, but no ^{40}Ar existed, so could not be degassed.

In fact, this paradox in the distribution of Ar isotopes in the Earth has been taken as evidence of a catastrophic degassing event shortly after the Earth was formed. Some suggest degassing resulted from formation of the Moon in a giant impact in the final stages of the Earth's accretion. (There is evidence from Xe isotopes produced by short–lived radioactive parent isotopes in the first few million years of Earth history that supports this theory).

Catastrophic early degassing of the Earth is easy to simulate in our model. In your spreadsheet, simply divide the initial abundance of ^{36}Ar, 4.0 x 10^{39} atoms, between the mantle and the atmosphere at t_0. For example, for 50% initial outgassing, set $^{36}Ar_{M,0}$ = 2 x 10^{39} atoms (cell C14), and $^{36}Ar_{A,0}$ = 2 x 10^{39} atoms (cell G14).

Q.16 How does this affect the final $^{40}Ar/^{36}Ar$ ratios of the mantle and atmosphere compared to all of your previous simulations?

Q.17 Set α_{Ar} back to a value that gives you the correct final atmospheric ^{40}Ar abundance.

Now try changing the degree of initial outgassing.

Can you find a value for the degree of initial outgassing that gives a mantle $^{40}Ar/^{36}Ar$ ratio > 1000 *and* an atmospheric $^{40}Ar/^{36}Ar$ ratio close to 295, the observed values?

Congratulations, you have just built a well-behaved planet. Better get to work on DNA and photosynthesis ....