

Isotope Geochem Notes: Rb-Sr, K-Ar and Ar-Ar Dating

Reading for this topic: White Lectures 5 and 6

Handout:

Guide questions:

Which isotope of Rb is unstable and to which isotope does it decay?

What is the general procedure for age dating rocks via the Rb-Sr method?

Which minerals are Rb-rich? Rb-poor? How do Rb and Sr reside in minerals?

For an igneous rock, what event does the age we get refer to? How is the “closing temperature” different for the Rb-Sr and K-Ar systems?

For a sedimentary rock, how can we ages for the source of the mineral grains or authigenic phases?

After you have plotted data on an isochron diagram, what simple test can help you eliminate bad age dates? What causes bad age dates?

Which naturally occurring isotope of K is unstable and to which isotopes does it decay?

Which minerals are K-rich? Which are K-poor?

What are the chemical properties of Ar?

What determines the smallest age that can be determined by K-Ar dating? Is this the same for all minerals or does it vary depending on the mineral?

How does one obtain a date for an igneous rock- what is the procedure for K-Ar and Ar-Ar methods?

With the Ar-Ar method, how can better ages be obtained from measurements taken as the crystals are heated stepwise?

Rb-Sr age dating

Practical procedure:

1) Collect samples- avoid weathered rock

2) Separate minerals

-Rb-rich phases: Biotite, muscovite, or Hornblende (note: easily weathered)

-Rb-poor: Plagioclase- Ca-bearing Feldspar

3) Dissolve minerals

4) Purify Sr- ion exchange chromatography

3) Measure Rb/Sr ratio (then calculate $^{87}\text{Rb}/^{86}\text{Sr}$)

4) Measure $^{87}\text{Sr}/^{86}\text{Sr}$ - via high-precision TIMS or ICP-MS

5) Plot an isochron: Plot $\frac{^{87}\text{Sr}}{^{86}\text{Sr}}$ vs. $\frac{^{87}\text{Rb}}{^{86}\text{Sr}}$, recall that $\frac{^{87}\text{Sr}}{^{86}\text{Sr}} = \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_0 + \frac{^{87}\text{Rb}}{^{86}\text{Sr}}(e^{\lambda t} - 1)$

...fit the data to a line. Slope = $(e^{\lambda t} - 1)$, Intercept is $\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_0$

THIS IS RATHER SLOW AND IS RARELY DONE TODAY. See Ar dating below for faster methods.

See Table 8.1 from Faure, 1986 text for list of Rb and Sr conc's in rocks.

Alternative: Use laser-ablation and analyze vapor from that- avoids digestion- still use isochrons. Much faster. Lesser precision, because Sr is analyzed along with the Rb, etc that ablates.

Isochrons give age dates of mineral solidification:

- 1) Igneous- reliable if you know all minerals grew from same liquid
May not work for late-stage plutonic rocks that may be hydrothermal- pegmatite
Granites “stew in their own juices” for millions of years
- 2) Metamorphic- minerals recrystallize, fluids carry Sr around
Can have complete resetting, all minerals with same new initial 87/86
See Fig. 8.5 from Faure, 1986.
Can also have partial resetting- a mess
Could also have minerals that grew slowly and/or at different times

Detecting problems with isochron dates:

- If minerals have been closed (no loss or gain), then all samples will fall on a single isochron (converse not necessarily true!)
- If minerals have gained or lost Rb or Sr: Assuming the loss/gain is not the same for the various minerals, linearity *probably* destroyed
Therefore: Poor linearity means a bad date!
In some cases, an isochron can be saved by removing one or two minerals that are known to be more easily reset or may have grown after the others

WHOLE-ROCK ISOCHRONS

- If isochrons for mineral separates are destroyed by metamorphism, there is some possibility that the length scale for redistribution of Rb + Sr is only a few cm- in this case, treat whole rocks as closed systems
- In other words: Instead of assuming each mineral is a closed domain, hypothesize that hand-sample size pieces of rock have remained closed overall (but the minerals within may have exchanged Rb and Sr with each other)
- Procedure: 1) Choose Rb-rich and Rb-poor rock types from same area
2) Grind up and homogenize whole rock samples from different rock types presumably formed from same event
3) Analyze these and plot an isochron –see **Fig. 8.7 from Faure, 1986**

SEDIMENTARY ROCKS: Difficult to date by any method

What event are we dating? Could be...

- 1) Formation of detrital grains... OR
 - 2) Age of authigenic minerals- grown after burial of the sediments.
- One approach: Concentrate on authigenic Illite (authigenic means grown in place)
-Illite: $KAl_4(Si_7AlO_{20})(OH)_4$ [Note muscovite: $K_2Al_4(Si_6Al_2O_{20})(OH)_4$]

-IMPORTANT: Rb usually follows K!!!

Or...Another mineral to try: Glauconitic phases- Fe-rich clays, formed shortly after sedimentation

Another approach... remove authigenic minerals, and try for an isochron on the detrital minerals (only works if they all came from the same source)

⁴⁰K decay and the K-Ar geochronometer

Overall decay const. for ⁴⁰K decay = 5.5×10^{-10}

Plenty left over from nucleosynthesis.

One of the important heat sources within the earth.

Branched decay: 10.5% to Ar, the rest to Ca. Seems like Ca would be good...

But... ⁴⁰Ca is very high in abundance and in most cases, the ingrowth of it is not measurable. When would you expect it *might* work?

**Important general principle: The ratio of ingrowth rate to initial amount present of the daughter isotope is critical.

K-Ar Age Dating

Very little Ar taken into crystals. Very high ingrowth/ initial ratio for K-rich crystals, and still high for K-poor phases or rocks.

Problems with leakage of Ar after production: Because Ar is a noble gas, it is present as Ar⁰ in crystals, and resides in defects. It can move rather easily through crystals because it does not form ionic bonds like Sr or Rb.

- 1) At high temperatures for all crystals
- 2) Even at low temperatures from some clay minerals
- 3) At moderate to low temperatures from very small crystals of any mineral

Examples of Ar dating: **DATING TOOL OF CHOICE FOR AGES IN THE 1 TO 200Ma range.**

- Routine dating of volcanic rocks
- Dating of sediments (e.g., hominid fossil-bearing layers in Kenya) using volcanic fragments within them
- Dating of the magnetic reversals- plate tectonics. Tying the magnetic record on land to an actual time scale, then using that to date the ocean floor.
- Dating of certain clay minerals

Practical procedure:

- 1) Collect samples
 - get fresh samples; weathering causes minerals to give up Ar and take some in from atm.
 - try to get rocks with high-K phases if you have a choice
 - volcanic glass is okay if fresh
 - plutonic rocks- may be messed up; post-solidification hydrothermal reactions and inherited Ar
- 2) Separate minerals OR do whole rock analyses if you must (less desirable)
 - minerals are better- individual crystals leak less
 - volcanic glass more likely have inherited Ar- from atm or magma
- 3) Measure [K] and calculate [⁴⁰K]
- 4) Measure [⁴⁰Ar]- melt crystals in a vacuum to release Ar
- 5) Often, some inherited Ar present, so measure ⁴⁰Ar/³⁶Ar and do the isochron method

Special Cases:

a) If you can assume the inherited Argon is from air:

$$\frac{{}^{40}\text{Ar}}{{}^{36}\text{Ar}} = \frac{{}^{40}\text{Ar}}{{}^{36}\text{Ar}}_{\text{air}} + \frac{\lambda_e}{\lambda} \frac{{}^{40}\text{K}}{{}^{36}\text{Ar}} (e^{\lambda t} - 1), \quad \text{where the air ratio} = 295.5$$

This looks like our standard isochron equation, but we know the intercept, and thus, only one measurement is needed to get an age. $\frac{\lambda_e}{\lambda}$ is there to account for the fact that only 10.5% of K decays go to Ar.

If the inherited Ar is not necessarily from air, you must use the full isochron approach.

b) If there's no inherited Ar (as revealed by lack of ${}^{40}\text{Ar}$) you can use:

$${}^{40}\text{Ar} = \frac{\lambda_e}{\lambda} {}^{40}\text{K} (e^{\lambda t} - 1)$$

What "event" are we dating?

What event "starts" this chronometer?

- Closure of the crystal w.r.t. Ar.

Closure temps of minerals:

- Ar moves through crystals more easily than ions (e.g., Sr^{2+}); not bound into the lattice.
- Relatively low closure temps, $\sim 200\text{-}700^\circ\text{C}$ (see Faure, 1986, Table 7.2)
- Possibility for some minerals to reset while others may not
- Possible for some domains of a single crystal to reset, others not (see below)

Ar-Ar dating: Most common method (K-Ar dating rarely used now)

- Convenient way to get the amount of ${}^{40}\text{K}$ as we measure ${}^{40}\text{Ar}$ - ONE ANALYSIS!!!
 - Actually, we determine ${}^{39}\text{K}$, and we know the ${}^{40}\text{K}/{}^{39}\text{K}$ ratio very well.
 - How it works: Bombard samples with neutrons...
 - Converts some of the ${}^{39}\text{K}$ to ${}^{39}\text{Ar}$ (neutron in, proton out, simultaneously)
 - ${}^{39}\text{Ar}$ half life is 269 years (samples are radioactive- a minor hassle)
- Measure on a mass spectrometer:

$${}^{40}\text{Ar}/{}^{39}\text{Ar}, \text{ this is related to time by: } \frac{{}^{40}\text{Ar}}{{}^{39}\text{Ar}} = C(e^{\lambda t} - 1), \quad \text{where } C' \text{ is a calibration}$$

constant that depends on the amount of neutron bombardment. One determines C' by analyzing standards along with the samples.

Step heating of minerals for Ar-Ar dating

20 years ago, they just melted the minerals in one step

Now, they use controlled heating by lasers to extract more information from minerals

Heat for a few seconds, then analyze Ar given off.

Successive pulses at successively greater power to get successively higher temperatures

At low temperatures, Ar comes out of more "open" or "leaky" domains

- The low-T steps are garbage- ignore

At high temperatures, Ar comes out of less open domains- better age dates

Comparison: K-Ar (Ar-Ar) dating versus Rb-Sr dating

- Rb-Sr dating not as common as Ar-Ar- more difficult.
- ^{87}Rb decay const = $1.42 * 10^{-11}$, 2x slower than ^{40}K
- Sr^{2+} fits into crystal lattice better than Ar, diffuses through lattice more slowly
 - Thus, **closure temp is essentially the crystallization temp**
- What is the main drawback of Ar dating?
 - Possible Ar loss. Rb-Sr is better in some cases.

Appendix: Diffusion of Ar and closure temperatures for Ar dating

What is the closure temp.? Consider the strong temperature dependence of diffusion:

Fick's Law; Diffusion Constant is D

But we know much about the systematics of diffusion:

The diffusion constant, $D = D_0 e^{-E_A/RT}$, E_A is the activation energy

Background: Activation energy is a term used in Kinetics. E_A is the amount of energy needed to get an atom "over the hump" so it can jump to a neighboring site. The $e^{-E_A/RT}$ term is a very common term in kinetics, and is used here to express the statistical probability that the activation energy at a given temperature, T

Energy barrier easier to cross at higher energy = higher temp.

Examples:

100°C increase in T leads to x100 increase in diffusion.

At room temperature, little Ar loss from small crystal in 1 Ga

- At 300°C, little loss
- At 400°C, minor loss over tens of Ma
- At 500°C, major loss over tens of Ma
- At 600°C, major loss over less than 1 Ma- useless.

Now... we also note that Ar loss from a crystal depends on its size

- Assuming a rod shape, loss is a function of Dt/a^2 (a = x-sect. Area)
- AND, crystals are full of defects
 - Diffusion of Ar through a crack or even a minor defect is very fast
- Thus, we can guess that there are large domains, where Ar retention is good, and others where it is not so good.

Example: Ar loss from a small domain, 1/10 the size of large one, is 100x greater.

Appendix: "Thermal Histories" of minerals

Thermal Histories: Goal is to determine the temperature history of the crystal over millions of years. This then tells us about the depth history of the rock. Example: How fast has material eroded off the top of the Himalaya.

Attempts have been made to correlate this quantitatively to derive thermal histories.

- Ages coming out of low-T laser pulses correspond to domains of the crystal that are more "open" and were open at the time given by that age

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- Ages coming out of the last pulse (melting pulse) correspond to the most closed domains. If there is a plateau, then we can guess there are some domains that record the age of the pluton
- If the plateau starts abruptly after the low-T garbage, then the whole crystal was reset at the same time (except for the very loosest domains)
- If there is a very broad slope up to the plateau, then the pluton must have cooled more slowly
- The shape of the curve can tell you if it was smooth or episodic cooling
- There are those who think they can calculate the cooling history, $T(t)$
- Here are two papers:
 - Thomson S. N., Stoeckhert B., and Brix M. R. (1998) **Thermochronology** of the high-pressure metamorphic rocks of Crete, Greece; **implications for the speed of tectonic processes**. *Geology (Boulder)* **26**(3), 259-262.
 - Vance D., Ayres M., Kelley S., and Harris N. (1998) **The thermal response of a metamorphic belt to extension**; constraints from laser Ar data on metamorphic micas. *Earth and Planetary Science Letters* **162**(1-4), 153-164.