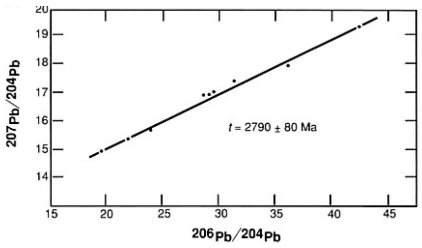


Dating processes

Reading: Fowler Ch 6

Earth's timeline

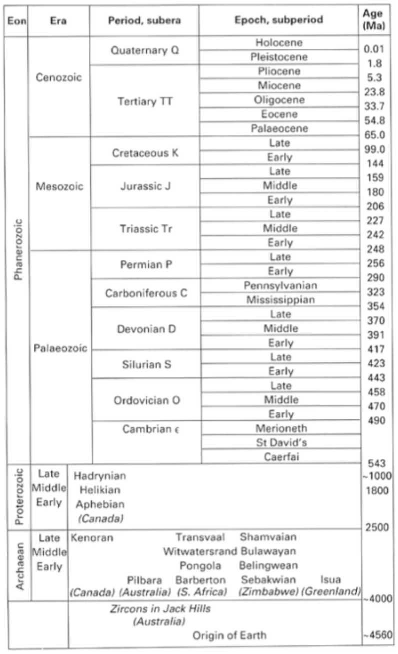
Stratigraphy and paleontology
➔ very precise relative ages

1896 Henri Becquerel discovered radioactivity

➔ the reason that Kelvin's estimate of the age of the Earth was an underestimate

1904 Rutherford and Boltwood developed radioactive dating

➔ absolute ages



Eon	Era	Period, subera	Epoch, subperiod	Age (Ma)
Phanerozoic	Cenozoic	Quaternary Q	Holocene	0.01
			Pleistocene	1.8
		Tertiary TT	Pliocene	5.3
			Miocene	23.8
			Oligocene	33.7
			Eocene	54.8
			Palaeocene	65.0
	Mesozoic	Cretaceous K	Late	99.0
			Early	144
		Jurassic J	Late	159
			Middle	180
			Early	206
		Triassic Tr	Late	227
			Middle	242
			Early	248
	Palaeozoic	Permian P	Late	256
			Early	290
		Carboniferous C	Pennsylvanian	323
			Mississippian	354
		Devonian D	Late	370
			Middle	391
			Early	417
		Silurian S	Late	423
			Early	443
		Ordovician O	Late	458
			Middle	470
			Early	490
		Cambrian ϵ	Merioneth	
			St David's	
			Caerfai	543
Proterozoic	Late	Hadrynian		~1000
	Middle	Helikian		1800
	Early	Aphebian *(Canada)*		2500
Archaean	Late	Kenoran	Transvaal Shamvaian	
	Middle		Witwatersrand Bulawayan	
	Early		Pongola Belingwean	
		Pilbara	Barberton Sebakwian Isua	
		(Canada) (Australia)	*(S. Africa) (Zimbabwe) (Greenland)*	~4000
		Zircons in Jack Hills (Australia)		
		Origin of Earth		~4560

Radioactive decay

The disintegration of a radioactive atom is a random event

- **the time of the decay is not affected by any process outside the atom**
- **the probability of decay in unit time is λ, the *decay constant***

number of atoms decayed:

$$\delta P = -\lambda P \delta t$$

where *P* is the number of atoms present

$$\frac{dP}{dt} = -\lambda P$$

integrate and define P_0 as the original number of atoms

$$P = P_0 e^{-\lambda t}$$

***half life*, $T_{1/2}$, when $P = P_0 / 2$**

$$T_{1/2} = \frac{\ln 2}{\lambda} = \frac{0.693}{\lambda}$$

A clock for rocks

***Parent* atom decays into a *daughter* atom ➔ at time *t*, $P = P_0 - D$**

$$P = P_0 e^{-\lambda t}$$

substitute $P = P_0 - D$

$$P_0 - D = P_0 e^{-\lambda t}$$

or…

$$D = P_0 \left(1 - e^{-\lambda t}\right)$$

substitute $P = P_0 e^{-\lambda t}$

$$D = P\left(e^{\lambda t} - 1\right)$$

rearrange…

$$t = \frac{1}{\lambda} \ln\left(1 + \frac{D}{P}\right)$$

the rock clock

By measuring the ratio of parent to daughter atoms in a mass spectrometer we can tell the age of the rock sample

….problems?

Geochronometers

Most common systems for dating geological samples

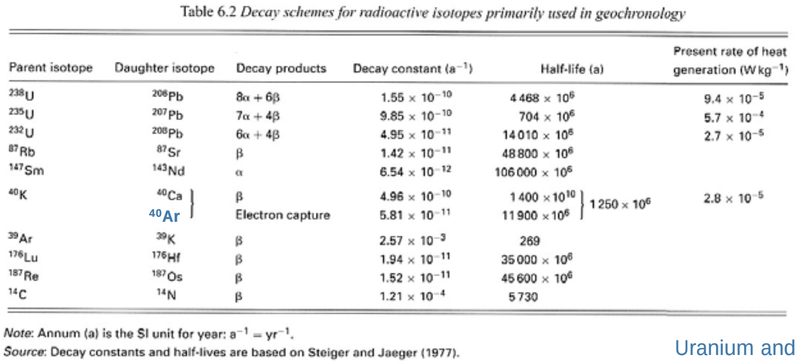


Table 6.2 *Decay schemes for radioactive isotopes primarily used in geochronology*

Parent isotope	Daughter isotope	Decay products	Decay constant (a^{-1})	Half-life (a)	Present rate of heat generation ($W\,kg^{-1}$)
^{238}U	^{206}Pb	$8\alpha + 6\beta$	1.55×10^{-10}	$4\,468 \times 10^6$	9.4×10^{-5}
^{235}U	^{207}Pb	$7\alpha + 4\beta$	9.85×10^{-10}	704×10^6	5.7×10^{-4}
^{232}U	^{208}Pb	$6\alpha + 4\beta$	4.95×10^{-11}	$14\,010 \times 10^6$	2.7×10^{-5}
^{87}Rb	^{87}Sr	β	1.42×10^{-11}	$48\,800 \times 10^6$	
^{147}Sm	^{143}Nd	α	6.54×10^{-12}	$106\,000 \times 10^6$	
^{40}K	^{40}Ca	β	4.96×10^{-10}	$1\,400 \times 10^{10}$ } $1\,250 \times 10^6$	2.8×10^{-5}
	^{40}Ar	Electron capture	5.81×10^{-11}	$11\,900 \times 10^6$	
^{39}Ar	^{39}K	β	2.57×10^{-3}	269	
^{176}Lu	^{176}Hf	β	1.94×10^{-11}	$35\,000 \times 10^6$	
^{187}Re	^{187}Os	β	1.52×10^{-11}	$45\,600 \times 10^6$	
^{14}C	^{14}N	β	1.21×10^{-4}	5 730	

Note: Annum (a) is the SI unit for year: $a^{-1} = yr^{-1}$.
Source: Decay constants and half-lives are based on Steiger and Jaeger (1977).

Uranium and potassium decay are responsible for most of the radioactive heat generation in the Earth

Best dates when use a system with a half life similar to the age of the sample

…why?

Element concentrations

need to have radiogenic elements present….

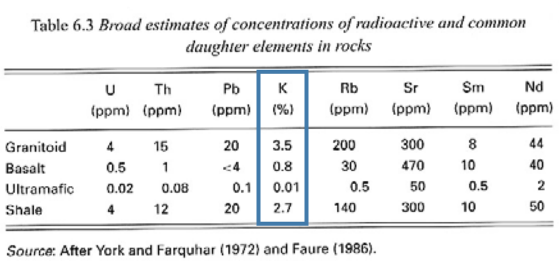


Table 6.3 *Broad estimates of concentrations of radioactive and common daughter elements in rocks*

	U (ppm)	Th (ppm)	Pb (ppm)	K (%)	Rb (ppm)	Sr (ppm)	Sm (ppm)	Nd (ppm)
Granitoid	4	15	20	3.5	200	300	8	44
Basalt	0.5	1	<4	0.8	30	470	10	40
Ultramafic	0.02	0.08	0.1	0.01	0.5	50	0.5	2
Shale	4	12	20	2.7	140	300	10	50

Source: After York and Farquhar (1972) and Faure (1986).

Potassium-Argon dating is possible for most rocks

Closed system?

1. **“Daughter” atoms deposited within parent rock**

   e.g. radiogenic Pb deposited with U by hydrothermal fluids

   what does this do to age estimates?

2. **Daughter atoms escaping**

   e.g. K decay to Ar (gas)

   ➔ products are only retained below the closure temperature

   We are dating the time the system becomes closed

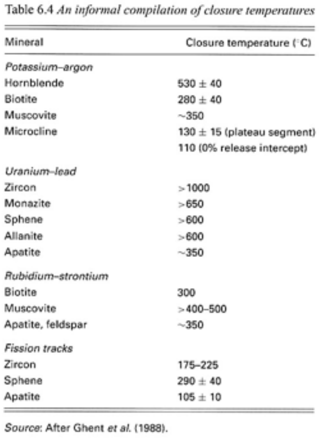


Table 6.4 *An informal compilation of closure temperatures*

Mineral	Closure temperature (°C)
Potassium–argon	
Hornblende	530 ± 40
Biotite	280 ± 40
Muscovite	~350
Microcline	130 ± 15 (plateau segment) 110 (0% release intercept)
Uranium–lead	
Zircon	>1000
Monazite	>650
Sphene	>600
Allanite	>600
Apatite	~350
Rubidium–strontium	
Biotite	300
Muscovite	>400–500
Apatite, feldspar	~350
Fission tracks	
Zircon	175–225
Sphene	290 ± 40
Apatite	105 ± 10

Source: After Ghent *et al.* (1988).

Rubidium-Strontium

^{87}Rb ➔ ^{87}Sr

$T_{1/2}$ = 48,800 Ma

^{87}Sr occurs naturally, in addition to being a decay product

$$[^{87}\mathrm{Sr}]_{now} = [^{87}\mathrm{Sr}]_0 + [^{87}\mathrm{Rb}]_{now}(e^{\lambda t} - 1)$$

Sr isotopes: 84 (0.6 %), 86 (10 %), 87 (7 %) and 88 (83 %)

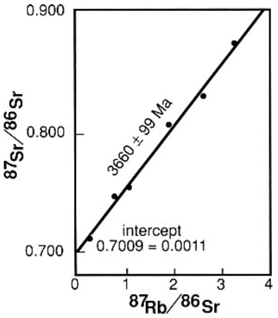
^{86}Sr is not a product of any decay sequence

$$\rightarrow [^{86}\mathrm{Sr}]_{now} = [^{86}\mathrm{Sr}]_0$$

normalize by $[^{86}\mathrm{Sr}]_{now}$

$$\frac{[^{87}\mathrm{Sr}]_{now}}{[^{86}\mathrm{Sr}]_{now}} = \frac{[^{87}\mathrm{Sr}]_0}{[^{86}\mathrm{Sr}]_0} + \frac{[^{87}\mathrm{Rb}]_{now}}{[^{86}\mathrm{Sr}]_{now}}(e^{\lambda t} - 1)$$

a straight line ➔



Measure the concentrations in various minerals or several samples

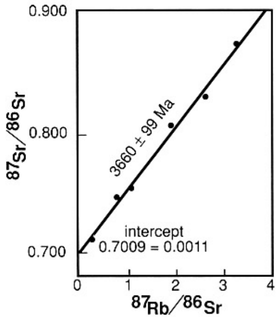
^{87}Rb ➔ ^{87}Sr
$T_{1/2}$ = 48,800 Ma

Rubidium-Strontium

$$\frac{[^{87}\mathrm{Sr}]_{now}}{[^{86}\mathrm{Sr}]_{now}} = \frac{[^{87}\mathrm{Sr}]_0}{[^{86}\mathrm{Sr}]_0} + \frac{[^{87}\mathrm{Rb}]_{now}}{[^{86}\mathrm{Sr}]_{now}} (e^{\lambda t} - 1)$$

a straight line ➔

Measure the concentrations in various minerals or several samples



Problems…

- assumes initial ratios the same
- Rb and Sr often mobile
- Rb is not abundant (particularly in limestones and ultramafics)
- Long half-life

Uranium-Lead

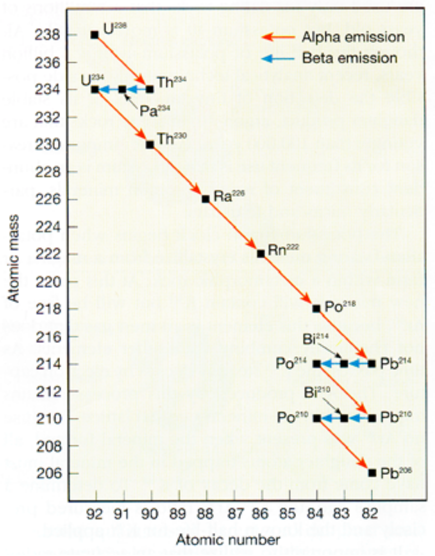
Three radioactive isotopes of U:

1. **^{238}U** (99.3% fractional abundance)
   14 step decay sequence to **^{206}Pb**

   still:

   $$[^{206}\mathrm{Pb}]_{now} = [^{238}\mathrm{U}]_{now}(e^{\lambda 238\, t} - 1)$$

   …why?



Uranium-Lead

Three radioactive isotopes of U:

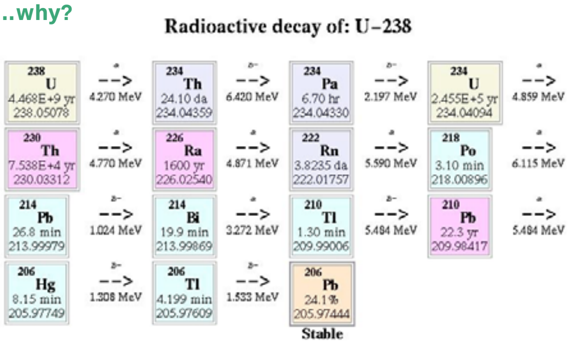
1. ^{238}**U** (99.3% fractional abundance)

   14 step decay sequence to ^{206}**Pb**

   still:

   $[^{206}\mathrm{Pb}]_{now} = [^{238}\mathrm{U}]_{now}(e^{\lambda 238\, t} - 1)$

…why?



Radioactive decay of: U–238

238 U 4.468E+9 yr 238.05078	a -->\ 4.270 MeV	234 Th 24.10 da 234.04359	b- -->\ 6.420 MeV	234 Pa 6.70 hr 234.04330	b- -->\ 2.197 MeV	234 U 2.455E+5 yr 234.04094	a -->\ 4.859 MeV
230 Th 7.538E+4 yr 230.03312	a -->\ 4.770 MeV	226 Ra 1600 yr 226.02540	a -->\ 4.871 MeV	222 Rn 3.8235 da 222.01757	a -->\ 5.590 MeV	218 Po 3.10 min 218.00896	a -->\ 6.115 MeV
214 Pb 26.8 min 213.99979	b- -->\ 1.024 MeV	214 Bi 19.9 min 213.99869	a -->\ 3.272 MeV	210 Tl 1.30 min 209.99006	b- -->\ 5.484 MeV	210 Pb 22.3 yr 209.98417	a -->\ 5.484 MeV
206 Hg 8.15 min 205.97749	b- -->\ 1.308 MeV	206 Tl 4.199 min 205.97609	b- -->\ 1.533 MeV	206 Pb 24.1% 205.97444 Stable			

Uranium-Lead

Three radioactive isotopes of U:

1. ^{238}**U** (99.3% fractional abundance)

   14 step decay sequence to ^{206}**Pb**

   still:

   $[^{206}\mathrm{Pb}]_{now} = [^{238}\mathrm{U}]_{now}(e^{\lambda 238\, t} - 1)$

2. ^{235}**U** (0.7% fractional abundance)

   decay sequence to ^{207}**Pb**

   $[^{207}\mathrm{Pb}]_{now} = [^{235}\mathrm{U}]_{now}(e^{\lambda 235\, t} - 1)$

3. ^{234}**U** (0.006% fractional abundance)

**As with the Rb-Sr series,
if no initial lead we can
use either of these series,
or we can combine…**

Uranium-Lead

take the ratio…

$$\frac{[^{207}Pb]_{now}}{[^{206}Pb]_{now}} = \frac{[^{235}U]_{now}(e^{\lambda 235\, t} - 1)}{[^{238}U]_{now}(e^{\lambda 238\, t} - 1)}$$

present day ration of radiogenic Pb isotopes

present day universal ratio = 1/137.88

half-lives known

➔ **measure the Pb ratio in one sample and can determine the age *if closed system***

Zircon is best / commonly used for this

- **common mineral**
- **retains U and daughter products**

Uranium-Lead **– Pb isotopes**

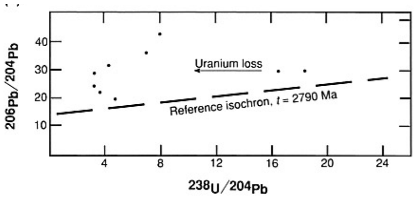
Pb isotopes: 204, 206, 207 and 208 – only 204 is non-radiogenic

Correct for initial unknown amount of Pb using ^{204}Pb concentration

$$\left[\frac{^{206}Pb}{^{204}Pb}\right]_{now} = \left[\frac{^{206}Pb}{^{204}Pb}\right]_0 + \left[\frac{^{238}U}{^{204}Pb}\right]_{now}\left(e^{\lambda_{238}t} - 1\right)$$

$$\left[\frac{^{207}Pb}{^{204}Pb}\right]_{now} = \left[\frac{^{207}Pb}{^{204}Pb}\right]_0 + \left[\frac{^{235}U}{^{204}Pb}\right]_{now}\left(e^{\lambda_{235}t} - 1\right)$$

➔ **plot uranium-lead isochrons just as in the rubidium-strontium case**



provided the uranium has not been lost….

Uranium-Lead – Pb isotopes

$$\left[\frac{^{206}Pb}{^{204}Pb}\right]_{now} = \left[\frac{^{206}Pb}{^{204}Pb}\right]_0 + \left[\frac{^{238}U}{^{204}Pb}\right]_{now} \left(e^{\lambda_{238}t} - 1\right)$$

$$\left[\frac{^{207}Pb}{^{204}Pb}\right]_{now} = \left[\frac{^{207}Pb}{^{204}Pb}\right]_0 + \left[\frac{^{235}U}{^{204}Pb}\right]_{now} \left(e^{\lambda_{235}t} - 1\right)$$

taking the ratio…

$$\frac{\left[^{207}Pb/^{204}Pb\right]_{now} - \left[^{207}Pb/^{204}Pb\right]_0}{\left[^{206}Pb/^{204}Pb\right]_{now} - \left[^{206}Pb/^{204}Pb\right]_0} = \left[\frac{^{235}U}{^{238}U}\right]_{now} \frac{e^{\lambda_{235}t} - 1}{e^{\lambda_{238}t} - 1}$$

➔ now we have a lead-lead isochron

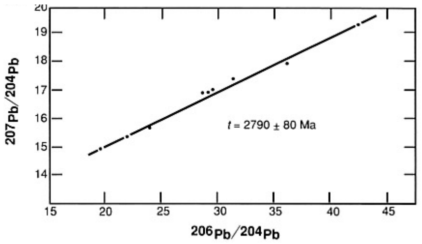
known ratio: 1/137.88

plot $[^{207}Pb/^{204}Pb]_{now}$ vs. $[^{206}Pb/^{204}Pb]_{now}$ …

Uranium-Lead – Pb-Pb isochron

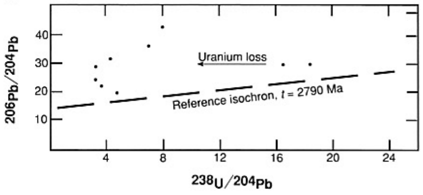
$$\frac{\left[^{207}Pb/^{204}Pb\right]_{now} - \left[^{207}Pb/^{204}Pb\right]_0}{\left[^{206}Pb/^{204}Pb\right]_{now} - \left[^{206}Pb/^{204}Pb\right]_0} = \left[\frac{1}{137.88}\right]_{now} \frac{e^{\lambda_{235}t} - 1}{e^{\lambda_{238}t} - 1}$$

plot $[^{207}Pb/^{204}Pb]_{now}$ vs. $[^{206}Pb/^{204}Pb]_{now}$ …



This is the same sample in which we had lost the U

➔ Pb is less mobile than U

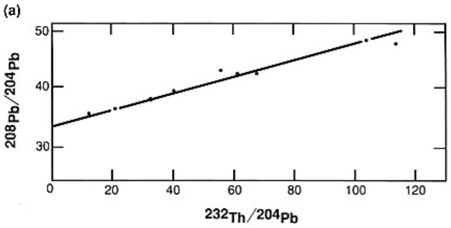


Thorium-Lead $^{232}Th \rightarrow {}^{208}Pb$

normalize by non-radiogenic ^{204}Pb as previously, and including the initial ^{208}Pb…

$$\left[\frac{^{208}Pb}{^{204}Pb}\right]_{now} = \left[\frac{^{208}Pb}{^{204}Pb}\right]_{0} + \left[\frac{^{232}Th}{^{204}Pb}\right]_{now}\left(e^{\lambda t}-1\right)$$

providing a Th-Pb isochron…

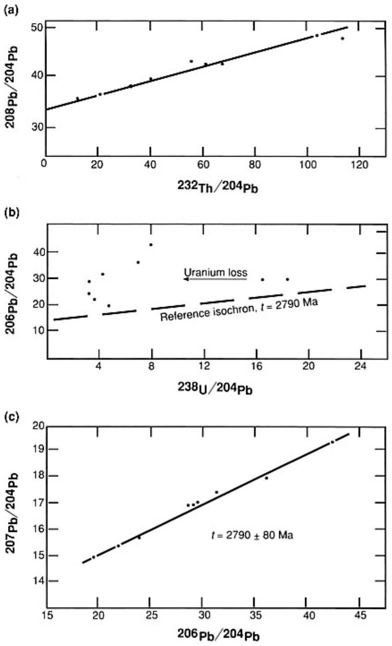


Th and Pb tend to be less mobile than U

➔ Th-Pb dating can be preferable

U and Th dating

Applying all these techniques to a single granite sample



(a) Th-Pb

- Some scatter in data (measurement error or small loss/gain of Th)
- Straight line provides age

(b) U-Pb

- Lots of scatter ➔ loss of U
- Otherwise would fall on 2790 Ma reference isochron

(c) Pb-Pb

- Points on a straight line with slope 0.1911 ➔ 2790 Ma

Typical example of problems that may be encountered with a sample

➔ apply multiple methods

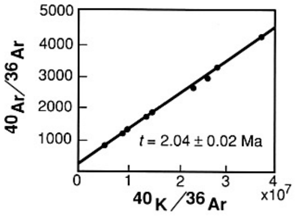
Potassium-Argon

Branched decay: ^{40}K $\to$ ^{40}**Ca** (β decay)
$\to$ ^{40}**Ar** (electron capture)

- **must account for the K to Ca decay**
- **normalize using non-radiogenic ^{36}Ar**

$$\left[\frac{^{40}Ar}{^{36}Ar}\right]_{now} = \left[\frac{^{40}Ar}{^{36}Ar}\right]_{0} + \left[\frac{^{40}K}{^{36}Ar}\right]_{now} \frac{\lambda_A}{\lambda_A + \lambda_C}\left(e^{(\lambda_A+\lambda_C)t} - 1\right)$$

➔ ***another* isochron diagram**



Advantages:

- Can assume $[^{40}Ar/^{36}Ar]_0$ was same as today's atmosphere (295.5) so only need single sample to get a date
- Shorter $T_{1/2}$ make it better for younger samples

But

- Ar is a gas, so mobile
- K also mobile

Argon-Argon

First irradiate sample in a nuclear reactor: ^{39}**K + n ➔ ^{39}Ar + p**

Also irradiate a sample, s, of known age, t_s, at the same time

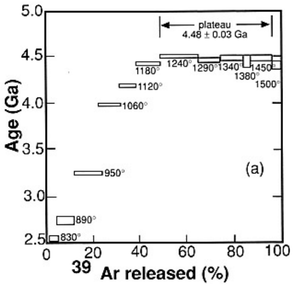
Then measure the ^{40}Ar-^{39}Ar ratio by heating the sample

$$\left[\frac{^{40}Ar}{^{39}Ar}\right]_{now} = \frac{\left(e^{(\lambda_A+\lambda_C)t} - 1\right)}{\left(e^{(\lambda_A+\lambda_C)t_s} - 1\right)}\left[\frac{^{40}Ar}{^{39}Ar}\right]_{now}^{s}$$

➔ the age is obtained from the two Ar ratios and the known age of sample s

Argon age spectrum for Menow meteorite

➔ heat sample stepwise measuring Ar ratios



Plateau at 50 % / 1240°
➔ age of sample 4.48 Ga

Temperature progression represents age vs. depth of metamorphic process
➔ get a time history

Samarium-Neodymium

^{147}Sm ➔ ^{143}Nd
$T_{1/2}$ = 106 Ga

Normalize with non-radiogenic ^{144}Nd

$$\left[\frac{^{143}Nd}{^{144}Nd}\right]_{now} = \left[\frac{^{143}Nd}{^{144}Nd}\right]_{0} + \left[\frac{^{147}Sm}{^{144}Nd}\right]_{now} \left(e^{\lambda t} - 1\right)$$

➔ isochron diagram

Advantages: Sm and Nd similar in chemical properties and little affected by metamorphism and weathering

Samarium-Neodymium

^{147}Sm ➔ ^{143}Nd
$T_{1/2}$ = 106 Ga

^{143}Nd concentrations on Earth have increased with time through decay of ^{147}Sm

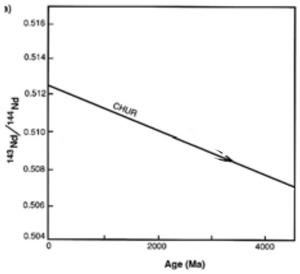
$$\left[\frac{^{143}Nd}{^{144}Nd}\right]_{0} = \left[\frac{^{143}Nd}{^{144}Nd}\right]_{now} - \left[\frac{^{147}Sm}{^{144}Nd}\right]_{now} \left(e^{\lambda t} - 1\right)$$

ratio at some time, t

ratio's today

For chrondritic meteorites today

= 0.512638 – 0.1967($e^{\lambda t}$ – 1)



➔ assume that the initial bulk concentration on Earth was the same as for chrondritic meteorites

➔ this is a model for the evolution of the primitive mantle

Samarium-Neodymium

^{147}Sm ➔ ^{143}Nd
$T_{1/2}$ = 106 Ga

When this primitive mantle melts

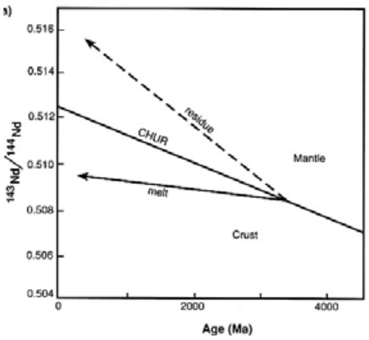
➔ the liquid will have lower Sm/Nd ratio and hence Nd/Nd ratio

➔ solid residual has the opposite effect

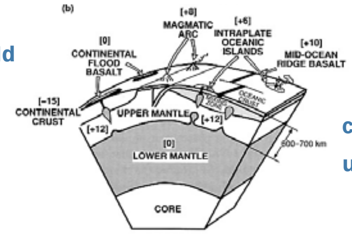
Define εNd

$$\varepsilon_{Nd} = \left(\frac{[^{143}Nd/^{144}Nd]_0}{[^{143}Nd/^{144}Nd]_0^{CHUR}} - 1 \right) \mathrm{x}10^4$$

normalize the initial Nd-ratio of a sample by the CHUR model at the same time



εNd



continental crust: -15

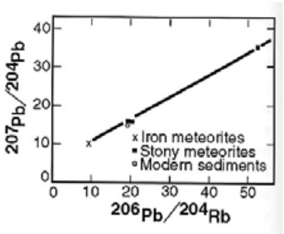
upper mantle: +12

Age of the Earth

Oldest rocks

- **Slave Province, NW Canada: zircons**
  3962 ± 3 Ma (U-Pb dates)
- **Isua supracrustal rocks, Greenland**
  3770 ± 42 Ma (Sm-Nd)
  3769 +11 -8 Ma (U-Pb on zircons)
- **Detrital zircons in Western Australia**
  4408 ± 8 Ma (U-Pb)

➔ continents in existence by 4400 Ma, 4000 Ma at the latest



For the Earth

- **Pb-Pb isochron for meteorites gives 4540 ± 70 Ma**