Vojtěch Janoušek:

Radiogenic isotope geochemistry and geochronology

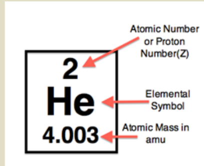
What is an isotope?

$${}^{A}_{Z}X$$

Nuclide

Z = *atomic number* = number of protons
A = *mass number* = number of nucleons (protons + neutrons)
N = *neutron number* = number of neutrons, i.e. $N = A–Z$

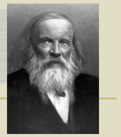
*The same Z – **isotopes***
*The same A – **isobars***



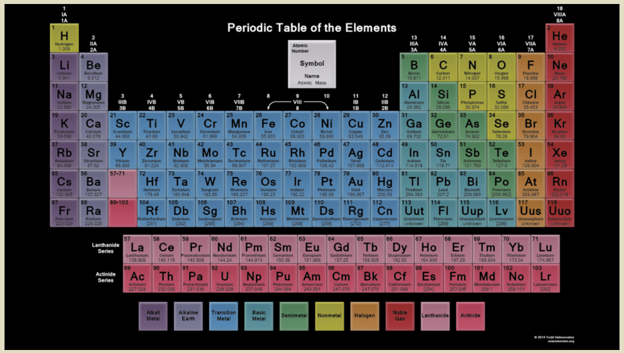
Relative atomic mass

- **Dalton (or atomic mass unit - a.m.u.)**
  = 1/12 of the mass of ^{12}C

Periodic table of elements



D.I. Mendeleev



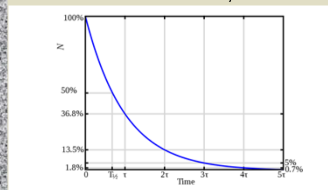
Radioactive decay

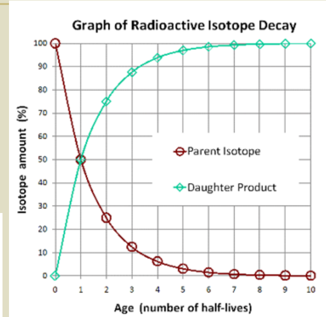
Decay constant *λ* reflects the stability of atoms = what is the proportion of atoms that decay in given time

$$N = N_0 e^{-\lambda t}$$

$$D = D_0 + N\left(e^{\lambda t} - 1\right)$$

Half-life $t_{1/2}$ = how long it takes for half of the atoms to decay

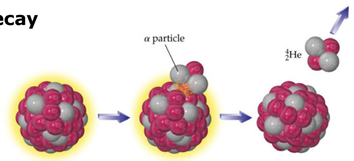




$$t_{1/2} = \frac{\ln 2}{\lambda} = \frac{0.693}{\lambda}$$

Types of radioactive decay

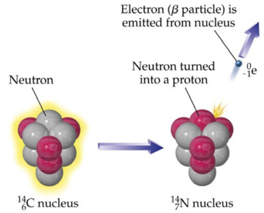
α decay



$$^{147}Sm \xrightarrow{\alpha} {}^{143}Nd$$

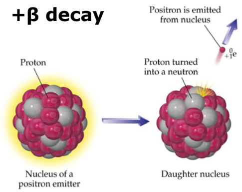
Types of radioactive decay

-β decay

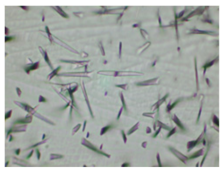


$$^{87}Rb \xrightarrow{-\beta} {}^{87}Sr$$
$$^{176}Lu \xrightarrow{-\beta} {}^{176}Hf$$
$$^{187}Re \xrightarrow{-\beta} {}^{187}Os$$

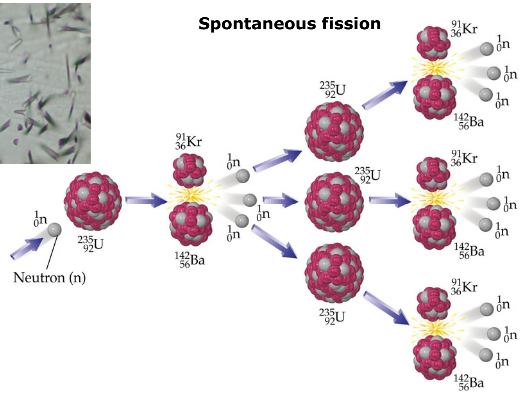
+β decay



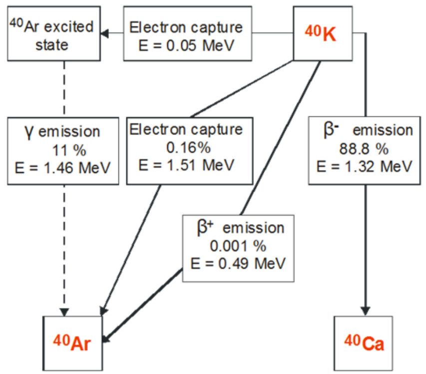
Types of radioactive decay



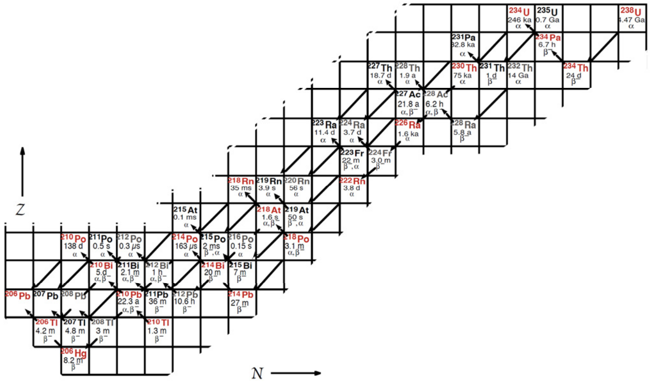
Spontaneous fission



Example of branched decay



Example of decay chain (^{238}U)



Calculating age and initial ratio

- **Radioactive isotope** (**^{87}Rb, ^{147}Sm, …**)
- **Radiogenic isotope** (**^{87}Sr, ^{143}Nd, …**)
- **Stable isotope** (**^{86}Sr, ^{144}Nd, …**)

- **R** (radioactive isotope to stable)
  e.g., (^{87}Rb/^{86}Sr) , (^{147}Sm/^{144}Nd)

  I (radiogenic isotope to stable)
  e.g., (^{87}Sr/^{86}Sr), (^{143}Nd/^{144}Nd)

Calculating age and initial ratio

$$I = I_i + R\left(e^{\lambda t} - 1\right)$$

$$\frac{^{143}Nd}{^{144}Nd} = \frac{^{143}Nd}{^{144}Nd}_i + \frac{^{147}Sm}{^{144}Nd}\left(e^{\lambda t} - 1\right)$$

$$\frac{^{87}Sr}{^{86}Sr} = \frac{^{87}Sr}{^{86}Sr}_i + \frac{^{87}Rb}{^{86}Sr}\left(e^{\lambda t} - 1\right)$$

$$\frac{^{176}Hf}{^{177}Hf} = \frac{^{176}Hf}{^{177}Hf}_i + \frac{^{176}Lu}{^{177}Hf}\left(e^{\lambda t} - 1\right)$$

$$\frac{^{187}Os}{^{186}Os} = \frac{^{187}Os}{^{186}Os}_i + \frac{^{187}\mathrm{Re}}{^{186}Os}\left(e^{\lambda t} - 1\right)$$

etc.

$$t = \frac{1}{\lambda}\ln\left(\frac{\frac{^{143}Nd}{^{144}Nd} - \frac{^{143}Nd}{^{144}Nd}_i}{\frac{^{147}Sm}{^{144}Nd}} + 1\right)$$

$$t = \frac{1}{\lambda}\ln\left(\frac{I - I_i}{R} + 1\right)$$

Radiogenic/radioactive/stable isotopes

Table 1 Decay schemes frequently used for geochronology and thermochronology.

Reaction	*Minerals*[a]	λ_p (yr^{-1})	$t_{1/2}$ (Gyr)[b]	*Source*
$^{147}Sm \rightarrow ^{143}Nd$	Grt, Cpx	6.54×10^{-12}	106.0	Lugmair and Marti (1978)
$^{87}Rb \rightarrow ^{87}Sr$	Ms, Bt, Phl, Kfs	1.42×10^{-11}	48.8	Steiger and Jäger (1977)
$^{176}Lu \rightarrow ^{176}Hf$	Grt	1.865×10^{-11}	37.2	Scherer *et al.* (2001)
$^{232}Th \rightarrow ^{208}Pb$[c]	Mz	4.9475×10^{-11}	14.0	Steiger and Jäger (1977)
$^{40}K \rightarrow ^{40}Ar$	Hbl, Ms, Bt, Phl, Kfs	5.8×10^{-11}	11.9	Steiger and Jäger (1977); Min *et al.* (2000)
$^{238}U \rightarrow ^{206}Pb$[c]	Zcn, Mz, Xn, Ttn, Rt, Ap	1.55125×10^{-10}	4.5	Steiger and Jäger (1977)
^{238}U fission	Zcn, Ap	$\sim 7 \times 10^{-10}$	~1.0	Naeser *et al.* (1989)
$^{235}U \rightarrow ^{207}Pb$[c]	Zcn, Mz, Xn, Ttn, Rt, Ap	9.8485×10^{-10}	0.7	Steiger and Jäger (1977)

[a] Abbreviations: Ap—Apatite; Bt—Biotite; Cpx—Clinopyroxene; Grt—garnet; Hbl—Hornblende; Kfs—K-feldspar; Ms—Muscovite; Mz—Monazite; Phl—phlogopite; Rt—rutile; Ttn—titanite; Xn—xenotime; Zcn—zircon. The half-life of a parent isotope, is equal to $0.693/\lambda_p$.
[b] $t_{1/2}$, the half-life of a parent isotope, is equal to $0.693/\lambda_p$. [c] These decay schemes also produce ^{4}He, forming the basis for (U–Th)/He geochronology (Equation (7)). Commonly analyzed minerals include Ap, Ttn, and Zcn.

Treatise on Geochemistry kap. 3.08: Geochronology and Thermochronology in Orogenic Systems (K. V. Hodges)

Rb–Sr method

Rubidium

- Alkali, lithophile element
- Substitutes for K
  (K-feldspars, micas, some clay minerals, evaporites…)

rubidium		*strontium*	
Isotopic composition (%)			
^{85}Rb ^{87}Rb	72.1654 27.8346	^{84}Sr ^{86}Sr ^{87}Sr ^{88}Sr	0.56 9.86 7.0 82.58
Relative atomic weight			
Rb	85.46776	^{84}Sr	83.9134
		^{86}Sr	85.9092
		^{87}Sr	86.9088
		^{88}Sr	87.9056

Strontium

- Alkaline earth; ion radius somewhat greater than that of Ca, substitutes for Ca (plagioclase, carbonates, apatite…), sometimes also K (K-feldspars)
- Rb is strongly incompatible element, thus its amount and Rb/Sr ratio rise with fractionation (esp. high in pegmatites)

Sr isotopes

^{87}Rb is −β radioactive:

$$^{87}Rb \rightarrow {}^{87}Sr + {}^{0}_{-1}e + \bar{\nu} + Q$$

λ = 1.42 . 10^{-11} yr^{-1}
(Steiger & Jäger 1977)

$$\frac{^{87}Sr}{^{86}Sr} = \frac{^{87}Sr}{^{86}Sr}_i + \frac{^{87}Rb}{^{86}Sr}\left(e^{\lambda t} - 1\right)$$

$$t = \frac{1}{\lambda}\ln\left(\frac{\frac{^{87}Sr}{^{86}Sr} - \frac{^{87}Sr}{^{86}Sr}_i}{\frac{^{87}Rb}{^{86}Sr}} + 1\right)$$

Rb–Sr method

Possible applications

- Cooling of plutonic rocks (blocking temperatures << solidus), crystallization of volcanic rocks (quick solidification)
- Dating of mineralization (using cogenetic minerals – muscovite, biotite, adularia)

Approx. blocking temperatures for Rb–Sr system:

orthoclase	320 °C
biotite	350 °C
muscovite	450–500 °C

Mezger (1990)

Appropriate material for Rb–Sr dating

- Mineral isochrons from plutonic rocks
  - K-rich minerals (high Rb/Sr): *K-feldspars (orthoclase, adularia), micas (muscovite, biotite, lepidolite), leucite*
  - Combined with Ca-rich minerals that are rather Rb poor (low Rb/Sr ratio): *plagioclase, apatite, ilmenite, amphibole, pyroxene*
- Whole-rock samples

Isochrons

Initial ratios are obtained

- Mineral lacking the radioactive element (e.g., apatite – contains nearly no Rb)
- Mineral extremely rich in radioactive element, soon dominated by the radiogenic component (e.g. lepidolite – rich in Rb)

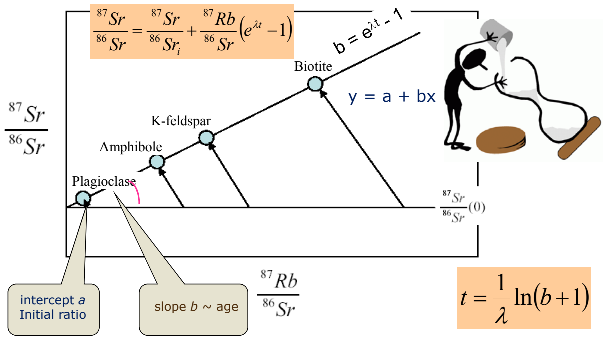
$$t = \frac{1}{\lambda}\ln\left(\frac{\frac{^{87}Sr}{^{86}Sr} - \frac{^{87}Sr}{^{86}Sr}_i}{\frac{^{87}Rb}{^{86}Sr}} + 1\right)$$

Isochron method

The samples define an isochron, if they:

- are cogenetic (identical source – thus share the same initial ratios)
- were contemporaneous (the same age)
- formed closed isotopic system throughout their history
- (there is a sufficient spread in compositions, i.e. in $^{87}Rb/^{86}Sr$ ratios)

Isochrons



Sm–Nd method

Samarium and neodymium

- Light Rare Earth Elements (LREE)
- LREE form own minerals (monazite, allanite, bastnäsite);
- Substitute for Ca^{2+} a Th^{4+} in rock-forming minerals (mainly plagioclase, biotite, apatite)
- Incompatible elements, i.e. concentrations of Sm and Nd increase with geochemical fractionation

samarium		*neodymium*	
Isotopic composition(%)			
^{144}Sm	3.1	^{142}Nd	27.13
^{147}Sm	15.0	^{143}Nd	12.18
^{148}Sm	11.3	^{144}Nd	23.80
^{149}Sm	13.8	^{145}Nd	8.30
^{150}Sm	7.4	^{146}Nd	17.19
^{152}Sm	26.7	^{148}Nd	5.76
^{154}Sm	22.7	^{150}Nd	5.64

Geochronologically significant is decay of ^{147}Sm:

$$^{147}Sm \xrightarrow{\alpha} {}^{143}Nd$$

$$\frac{^{143}Nd}{^{144}Nd} = \frac{^{143}Nd}{^{144}Nd}_i + \frac{^{147}Sm}{^{144}Nd}(e^{\lambda t} - 1)$$

$\lambda = 6.539 \times 10^{-12}\ yr^{-1}$
(Lugmair & Marti 1978)

Sm–Nd method

Possible dating applications

- Cooling of basic intrusions
- Crystallization of basic volcanic rocks (rapid cooling) – they are difficult to date by the Rb/Sr and U/Pb methods (especially if very old, partly altered and do not contain zircon)
- Dating high-grade metamorphism (granulite- and eclogite-facies)

Appropriate material for Sm–Nd dating

- Minerals from (ultra-)basic igneous rocks

  pyroxene, amphibole, plagioclase, ilmenite, apatite, monazite, zircon…
- Garnet (+ Cpx) in metamorphic rocks
- Whole-rock samples

Sm–Nd method

- Evolution of terrestrial Nd is explained by the model of a primitive mantle reservoir with Sm/Nd ratio of chondritic meteorites, so-called **CHUR** (*Chondritic Uniform Reservoir* or *Bulk Earth*: *DePaolo 1988*) with present-day isotopic composition:

$^{147}Sm/^{144}Nd_{CHUR} = 0.1967$
$^{143}Nd/^{144}Nd_{CHUR} = 0.512638$
(Jacobsen & Wasserburg 1980)

Small differences in $^{143}Nd/^{144}Nd$ ratios → initial composition of the Nd is normally expressed using the ε_{Nd} notation

$$\varepsilon^i_{Nd} = \left[\frac{\left(\frac{^{143}Nd}{^{144}Nd}\right)^{SA}_i}{\left(\frac{^{143}Nd}{^{144}Nd}\right)^{CHUR}_i} - 1\right] \times 10^4$$

Where:
index „i" denotes initial ratio, SA = sample

Nd isotopes

trivalent REE – ***lanthanide contraction***, Nd shows greater ionic radius than Sm and thus the ratios Sm/Nd decrease during geochemical fractionation; this fractionation is still comparably limited

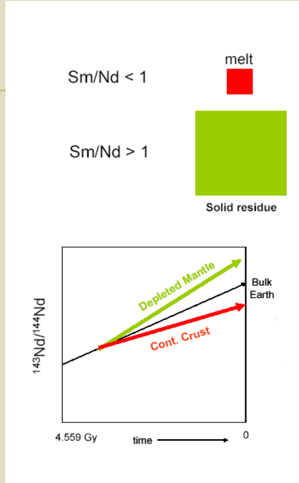
Parcial melting of CHUR

Melt — depleted in Sm,
Sm/Nd ratio is lower than that of CHUR

Residue — enriched in Sm,
higher Sm/Nd ratio

The melt-depleted mantle domains develop, over time, $^{143}Nd/^{144}Nd$ greater than CHUR

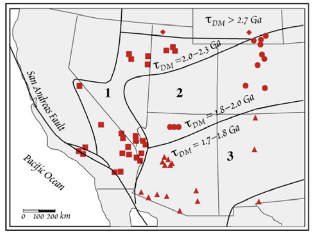
(so-called **Depleted Mantle**, DM – *DePaolo 1988*)



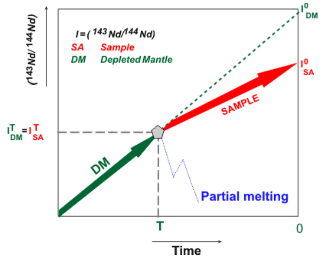
Nd model ages

Sm/Nd decreases during differentiation , thus mantle develops higher $^{143}Nd/^{144}Nd$ than crust

Model age = moment in the past when Nd isotopic composition of the sample was identical with that of some model reservoir (most often **CHUR** or Depleted Mantle — **DM**).



Isotopic provinces of the Western U.S. based on crustal residence times (T_{DM})
(Bennett and DePaolo 1987)



Lu–Hf method

Lutetium

- The heaviest among REE
- Enters the crystal structure of many accessories: allanite, monazite, apatite and titanite

lutetium		***hafnium***	
Isotopic composition (%)			
^{175}Lu	97.4	^{174}Hf	0.16
^{176}Lu	2.6	^{176}Hf	5.2
		^{177}Hf	18.6
		^{178}Hf	27.1
		^{179}Hf	13.7
		^{180}Hf	35.2

Hafnium

- Transition metal
- Geochemical behaviour strongly resembles Zr, for which it readily substitutes in accessory minerals (zircon)
- ^{176}Lu shows branched decay:

1 **-β emission**
(97 % of decays)

$$^{176}Lu \xrightarrow{-\beta} {}^{176}Hf + \gamma$$

l = 1.94×10^{-11} yr^{-1}
(Patchett & Tatsumoto 1980)

2 **Electron capture** (3 % of decays)
no geochronological meaning

Lu–Hf method

Appropriate material for Lu–Hf dating

- Usage analogous to the Sm–Nd method
- Shorter half life and higher Lu/Hf ratios of common rocks and minerals result in greater variability of the Hf isotopic composition (= advantage)

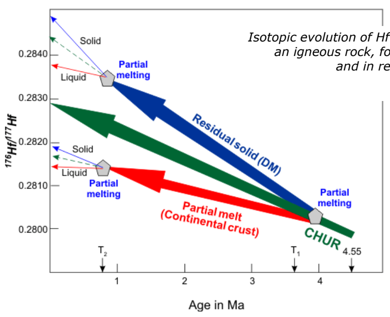
Mineral phases in igneous and metamorphic rocks

- High Lu/Hf: titanite, apatite, monazite, allanite
- Low Lu/Hf: **zircon** = ideal mineral for Hf isotopic studies:
  - Hf substitutes into the crystal lattice (and is thus relatively immobile)
  - High concentrations of Hf and low Lu/Hf ratios in zircon require (almost) no age correction for the initial ratios
  - Is often combined with *in situ* U–Pb dating, mostly using LA ICP-MS

Whole-rock samples

- Acid as well as basic
(Lu/Hf ratio decreases with geochemical fractionation)

Lu–Hf method



Isotopic evolution of Hf in a chondritic reservoir, in an igneous rock, formed by its partial melting, and in residue of this partial melting (Faure 1986)

$^{176}Lu/^{177}Hf_{CHUR}$ = 0.0334 a $^{176}Hf/^{177}Hf_{CHUR}$ = 0.28286

(Patchett & Tatsumoto 1980)

Lu–Hf method

Petrogenesis of igneous rocks

Small differences in $^{176}Hf/^{177}Hf$ → initial ratios of Hf isotopes are usually expressed as:

$$\varepsilon^{i}_{Hf} = \left(\frac{\left(\frac{^{176}Hf}{^{177}Hf}\right)^{SA}_{i}}{\left(\frac{^{176}Hf}{^{177}Hf}\right)^{CHUR}_{i}} - 1 \right) \times 10^4$$

Where: index „i" = initial ratio, SA = sample, CHUR = Chondritic Uniform Reservoir

$\varepsilon_{Hf} < 0$: rock originated from (or assimilated significant amount of) material with Lu/Hf lower than CHUR (e.g., old crustal rocks).

$\varepsilon_{Hf} > 0$: rock comes from a source with high Lu/Hf (e.g. mantle domains impoverished in incompatible elements due to previous partial melting – Depleted Mantle = DM)

K–Ar and Ar–Ar methods

Potassium

- Alkali metal
- Lithophile element (8th most common in the Earth's crust)
- Three naturally occurring isotopes: ^{39}K, ^{40}K, ^{41}K

Argon

- 2nd most common noble gas
- Three naturally occurring isotopes: ^{36}Ar, ^{38}Ar, ^{40}Ar

potassium		*argon*	
Isotopic composition (%)			
^{39}K ^{40}K ^{41}K	93.2581 0.01167 6.7302	^{36}Ar ^{38}Ar ^{40}Ar	0.337 0.063 99.600
Relative atomic mass			
A_r(K)	39.098304	A_r(Ar)	39.9476

K–Ar and Ar–Ar methods

^{40}K is radioactive with branched decay

1. **-β emission** (88.8 % of decays)

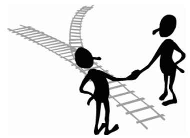
   $^{40}K \rightarrow {}^{40}Ca + {}^{0}_{-1}e$ λ_β = 4.962 . 10^{-10} yr^{-1}

2. **Electron capture** (11.16 % of decays)

   $^{40}K + {}^{0}_{-1}e \rightarrow {}^{40}Ar \pm \gamma$ λ_{EC} = 0.581 . 10^{-10} yr^{-1}

3. **+β emission** (0.001 % of decays)

   $^{40}K \rightarrow {}^{40}Ar + {}^{0}_{+1}e + 2\gamma$

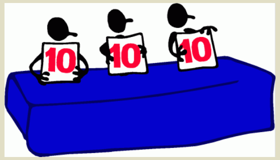


Total decay constant for ^{40}K:
$\lambda = \lambda_{EC} + \lambda_\beta$ = 5.543 . 10^{-10} yr^{-1}

K–Ar method

Reasonable age by the K–Ar method can be obtained if:

- Mineral has represented a closed system for ^{40}Ar and potassium throughout the history
- Amount of extraneous ^{40}Ar is negligible or can be reasonably corrected for
- Potassium isotopic composition is normal and has not changed due to fractionation (relatively light element)



K–Ar method

Argon loss is caused usually by:

- Regional metamorphism (increased P–T, recrystallization)
- Increased T or even partial melting due to contact metamorphism
- Inability of the crystal lattice to retain Ar (even at low P–T)
- Chemical weathering and hydrothermal alteration
- Dissolution and reprecipitation of the evaporites
- Mechanical breakage of the minerals (even gridding!)
- Lattice damage by the radioactive decay

K–Ar method

Non-radiogenic Ar

Extraneous Ar

- ***Inherited Ar***
  (originated in the rock by radioactive decay before the dated event)
- ***Excess Ar***
  (captured by minerals due to diffusion from surroundings)
- Ar can be captured esp. by minerals with large hollows in their structure (beryl, cordierite, tourmaline, often also pyroxene)

Atmospheric Ar

- Ar gained from atmosphere
  (adsorption at the grain boundaries, microcracks)

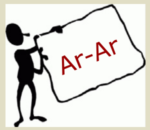
Ar–Ar method

Ar–Ar method

- Modification of the classic K–Ar technique
- Sample irradiation by fast neutrons in a nuclear reactor:

^{39}K (n,p) ^{39}Ar, i.e.:

$$^{39}_{19}K + ^{1}_{0}n \rightarrow ^{39}_{18}Ar + ^{1}_{1}p$$



- Thus produced ^{39}Ar is analysed in the same fraction as ^{40}Ar →
  it eliminates the problems with sample inhomogeneity, easier analytics
- *Incremental heating technique* or *laser ablation*:
  - useful for samples that suffered a partial Ar loss
  - (*in situ* measurement)

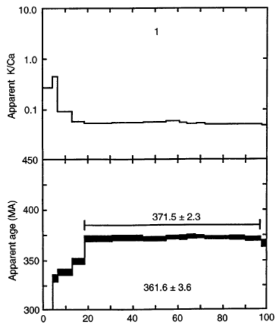
Ar–Ar method

Using Ar–Ar method of dating

- Fresh, unaltered samples
- Binary plots of fraction of the released Ar (0–100 %) vs. $^{40}Ar/^{39}Ar$
- Dating of volcanic rocks, including pyroclastics (phenocrysts of K-rich minerals, e.g. K-feldspar, micas, amphibole) – stratigraphy
- Low blocking temperatures of Ar–Ar system in minerals – ‚*cooling ages*'

Approx. blocking temperatures for K(Ar)–Ar system:	
amphibole	500–450 ºC
muscovite	350–400 ºC
biotite	300 ºC
microcline	150–200 ºC

Mezger (1990)



Amphibole from metagabbro, Mariánské Lázně Complex, Czech Rep. (Dallmeyer & Urban 1998)

Re–Os method

Rhenium

- Transition metal
- Rare in rock-forming minerals, more common in sulphides or REE minerals

rhenium		*osmium*	
Isotopic composition (%)			
^{185}Re	37.4	^{184}Os	0.02
^{187}Re	62.6	^{186}Os	1.58
		^{187}Os	1.6
		^{188}Os	13.3
		^{189}Os	16.1
		^{190}Os	26.4
		^{192}Os	41.0

Osmium

- Transition metal from the Pt group (PGE)
- Bothe elements are chalcophile and siderophile, i.e. are concentrated in sulphidic phase (with iron)

^{187}Re is -β radioactive:

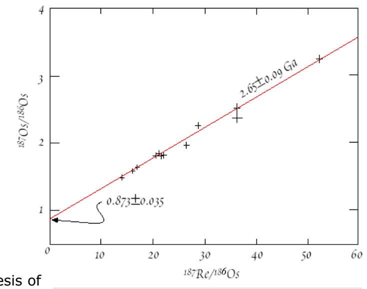
$$^{187}Re \xrightarrow{-\beta} {}^{187}Os$$

l = 1.64×10^{-11} yr^{-1} *(Lindner et al. 1989)*

Re–Os method

Isochron method

$$\frac{^{187}Os}{^{186}Os} = \frac{^{187}Os}{^{186}Os_i} + \frac{^{187}Re}{^{186}Os}\left(e^{\lambda t} - 1\right)$$



Re–Os isochron for komatiites from Monro Township (Walker et al. 1989)

Possible application

- Dating of sulphide deposits
- Dating of iron meteorites
- Geochronology and petrogenesis of ultrabasic rocks (esp. Precambrian)
- Mineral phases rich in Re and poor in Os
- Especially sulphides – molybdenite, PGE minerals

http://www.geo.cornell.edu/geology/classes/Geo656/656home.html

Re–Os method

Evolution of terrestrial Os

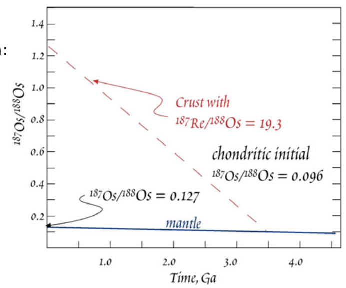
- Present-day CHUR composition:

  $^{187}Re/^{186}Os_{CHUR}$ = 3.3

  $^{187}Os/^{186}Os_{CHUR}$ = 1.06

  (Walker et al. 1989)

- **Re** is incompatible element, i.e. is concentrated in melt
- **Os** is strongly compatible element, and thus remains in the residue after melting
- During differentiation, the Re/Os ratio increases, and therefore the mantle develops to (much) lower $^{187}Os/^{186}Os$ then the crust



Theoretical evolution of Os isotopes in chondritic mantle and continental crust (Allegre & Luck 1980)

http://www.geo.cornell.edu/geology/classes/Geo656/656home.html

Pb isotopes

Uranium

- With Th belong to actinides
- Three naturally occurring isotopes
- ^{235}U and ^{238}U are radioactive and form decay chains with ^{207}Pb and ^{206}Pb as end products
- ^{234}U is intermediate product of the ^{238}U decay chain

Thorium

- Six naturally occurring isotopes; only ^{232}Th has a long half-life
- ^{232}Th forms a decay chain with ^{208}Pb as an end product
- Isotopes 227, 228, 230, 231 and 234 are intermediate members of decay chains of ^{232}Th, ^{235}U and ^{238}U

uranium		***lead***	
Isotopic composition (%)			
^{234}U ^{235}U ^{238}U	0.0057 0.7200 99.2743	^{204}Pb ^{206}Pb ^{207}Pb ^{208}Pb	1.4 24.1 22.1 52.4

$$^{238}U \longrightarrow {}^{206}Pb$$

$$^{235}U \longrightarrow {}^{207}Pb$$

$^{238}U/^{235}U = 137.88$

$$^{232}Th \longrightarrow {}^{208}Pb$$

^{204}Pb is non-radiogenic isotope

$$\mu = \frac{^{238}U}{^{204}Pb}$$

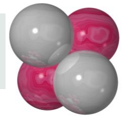
U–(Th)–Pb dating of accessory phases

Concordant ages

t($^{207}Pb/^{206}Pb$) = t($^{207}Pb/^{235}U$) = t($^{206}Pb/^{238}U$) = t($^{208}Pb/^{232}Th$)

Discordant ages

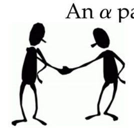
- Lead loss from damaged crystal lattice
- Gain of U or Th



An α particle

Concordia = a curve onto which fall all the concordant analyses:

t($^{207}Pb/^{235}U$) = t($^{206}Pb/^{238}U$)



Concordia diagram

Wetherill graph

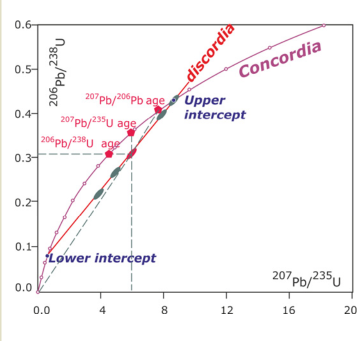
$^{207}Pb^*/^{235}U$–$^{206}Pb^*/^{238}U$

(Concordia diagram)

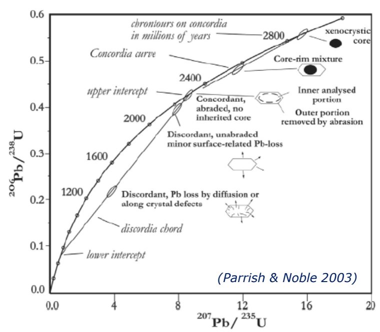
- Used for U-rich accessories: zircon, monazite, titanite, apatite, rutile…)
- $^{207}Pb^*$, $^{206}Pb^*$= radiogenic Pb (corrected for non-radiogenic, ‚common' lead) e.g. by model of Stacey & Kramers (1975)

$$\frac{^{206}Pb^*}{^{238}U} = \left(e^{\lambda_1 t} - 1\right)$$

$$\frac{^{207}Pb^*}{^{235}U} = \left(e^{\lambda_2 t} - 1\right)$$



Interpretation of discordant data

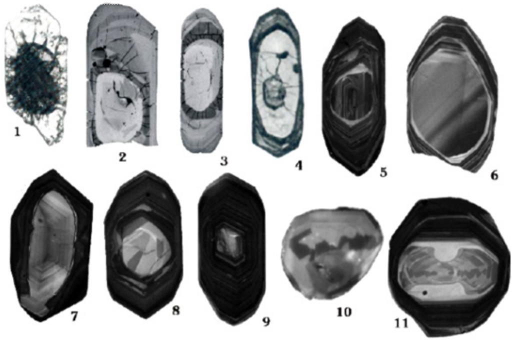


(Parrish & Noble 2003)

Internal structure of the zircon crystals

- **BSE** (*back-scattered electrons*)
- **CL** (*cathodoluminescence*)

Corfu et al. (2003)



SHRIMP

SHRIMP = Sensitive High-resolution Ion MicroProbe

- *in-situ* analysis, secondary beam of Pb ions triggered by bombardment of the sample by light ions (such as oxygen) (SIMS)

Advantages

- Dating directly in the thin section
- Dating of individual zones of zircon crystals
- (In combination with CL, BSE) – dating zircons with complex inheritance, from polymetamorphic terrains with complex history
- High spatial resolution (~10–20 μm)

Disadvantages

- Complex instrumentation (interferences)
- Slow (1 pt. ~ 30 min.)
- Expensive, not easily accessible

LA ICP-MS

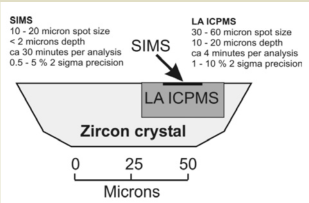
LA ICP-MS
(Laser-Ablation Inductively-Coupled Plasma Mass-Spectrometry)

Advantages

- Dating directly in the thin section
- Dating of individual zones of zircon crystals
- Much cheaper than SHRIMP
- Much quicker (1 pt. ~ several min)

Disadvantages

- Complex instrumentation
- Lower spatial resolution than SHRIMP



Comparison of SHRIMP (SIMS) and LA ICP-MS dating of zircon (Košler & Sylvester 2003)

Dating monazite by electron microprobe

Chemical dating of monazite by electron microprobe *(Suzuki et al. 1994)*

$$Pb = \frac{Th}{232}\left[e^{\lambda_{232}t} - 1\right]208 + \frac{U}{238.04}0.9928\left[e^{\lambda_{238}t} - 1\right]206 + \frac{U}{238.04}0.0072\left[e^{\lambda_{235}t} - 1\right]207$$

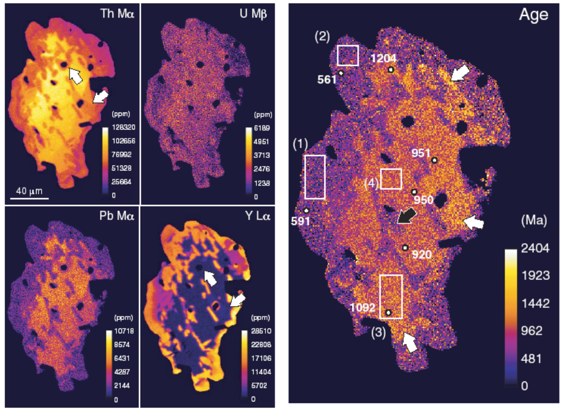
(Montel et al. 1996)

Advantages

- Dating directly in the thin section
- Extremely quick and cheap method, ideal for study of unknown (polymetamorphic) terrains, sediment provenance
- High spatial resolution several μm)

Disadvantages

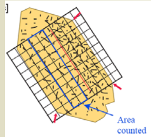
- Imprecise
- All Pb is considered to be radiogenic
  (no correction on 'common lead' can be applied)

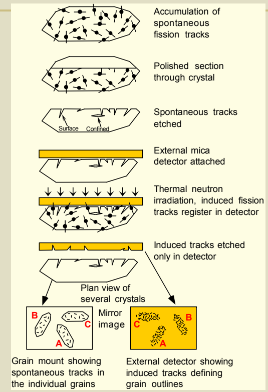


(Goncalves et al. 2005)

Fission track method

- Method based on natural decay of uranium by spontaneous fission of ^{238}U.
- Counting the number of fission tracks in natural sample. It is proportional to the U concentration, age and the well-known decay constant.
- The U concentration is obtained from the proportion of induced fission-tracks after irradiation with thermal neutrons in a nuclear reactor or is measured directly (e.g. by LA ICP MS).
- Dating cooling of accessory minerals, e.g. apatite, zircon, titanite





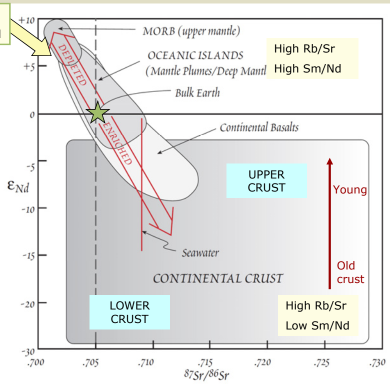
Using Sr–Nd isotopes I. – magma sources

ε_{Nd} < 0

Rock originated from (or assimilated much material derived from) a source with Sm/Nd ratio lower than CHUR (e.g., old crust)

ε_{Nd} > 0

Rock comes form a source with high Sm/Nd (e.g., mantle depleted by the previous extraction of basaltic magma; Depleted Mantle = DM)



http://www.geo.cornell.edu/geology/classes/Geo656/656home.html

Processes determining/modifying the composition of magmatic rocks

Closed system

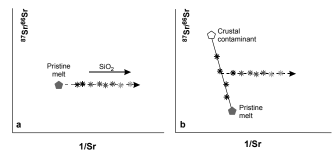
The magma develops without any exchange of material with the surroundings (

- Fractional crystallization, crystal accumulation…
- Isotopic composition still reflects that of the source

Open system

Isotopic composition of the source is not preserved as a result of:

- *Hybridization* (*magma mixing*)
- *Contamination* by country rocks (often in the form of AFC)
- Late *alterations*



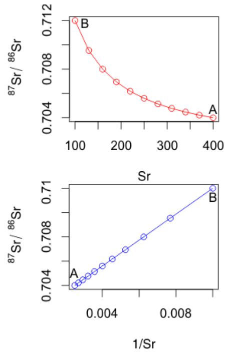
*Development of $^{87}Sr/^{86}Sr$ composition in a fractionating mantle-derived igneous suite. **a** Closed-system fractional crystallization, **b** Contamination, followed by closed-system fractionation (after Briquet & Lancelot 1979)*

Pb isotopes

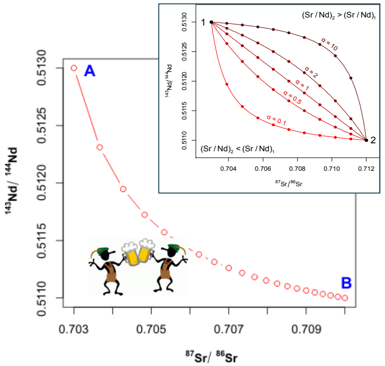
- *Continental crust* shows much higher average U, Th and Pb concentrations than mantle (> 10 ppm Pb in continental crust vs. < 1 ppm Pb in Earth's mantle);
- This in principle applies also to *oceanic crust*, including the marine sediments

- Therefore, Pb isotopes = highly sensitive indicator of crustal contamination
- Currently 93.7% of natural U is ^{238}U, therefore the $^{206}Pb/^{204}Pb$ is the ratio of choice to examine the crustal contamination of mantle-derived magma

Using Sr–Nd isotopes II. – binary mixing



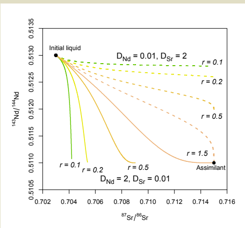
(A: Sr = 400 ppm; B: Sr = 100 ppm)

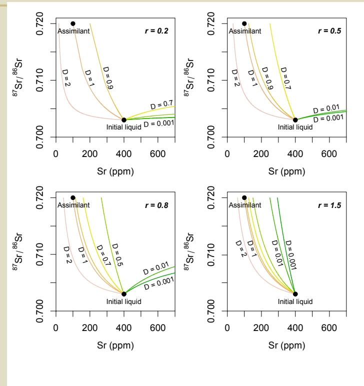


(A: Sr = 100 ppm, Nd = 2 ppm; B: Sr = 200 ppm, Nd = 20 ppm)

Using Sr–Nd isotopes III. – AFC

- Composition of the resulting magma does not plot onto a tie line between both end members, unlike in the case of binary mixing.





Diffusion

1. Grain-boundary diffusion

- (relatively quick) transport in fluid phase

2. Volume diffusion

- (relatively slow) material transport through the crystal lattice
- compensates the gradient of concentration, temperature or chemical potential
- speeded up by the presence of crystal lattice imperfections (dislocations, vacancies)

Fick's (First) Law: $$J = -D\frac{\partial c}{\partial x}$$

J = material flux, D = diffusion coefficient, c = concentration, x = distance

($\frac{\partial c}{\partial x}$ = concentration gradient)

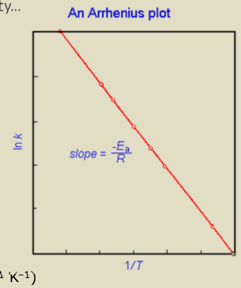
Diffusion

Diffusion coefficient **depends on**:
P, T, aH_2O, fO_2, anisotropy of the lattice, porosity…

Arrhenius equation:

$$D = D_0 e^{-E_a/RT}$$

$$\ln D = \ln D_0 - \frac{E_a}{RT}$$



D = diffusion coefficient
D_0 = frequency factor ($m^2 s^{-1}$)
E_A = activation energy ($J\ mol^{-1}$)
T = temperature (K)
R = Universal Gas Constant (R = 8.31441 $J\ mol^{-1}\ K^{-1}$)

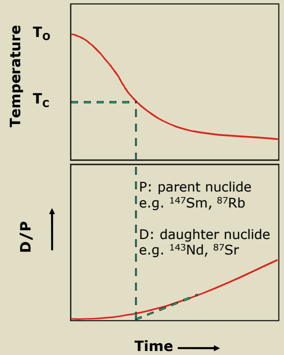
Blocking temperatures

Blocking/closure temperatures

- Closure of isotopic system (relative to both the parent and daughter isotopes)
- Usage: PTt paths

Open system
(*Dodson 1973, 1976*)

- Linear decrease in temperature
- Cooling mineral exchanges isotopes with the rest of rock, that acts as an infinite reservoir



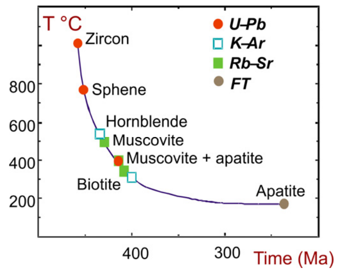
Blocking temperatures

$$T_C = \frac{R/E_A}{\ln\left(\frac{A\tau D_0}{a^2}\right)}$$

a = characteristic diffusion size (~ grain radius)
A = geometry factor (sphere = 55, cylinder =27, plate = 8.7)
τ= time constant (with which the diffusion coefficient diminishes)

Blocking temperature is not a constant but depends on:

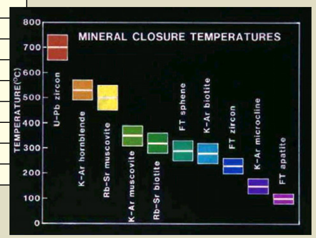
- Mineral
- Grain size
- Shape of the grain
- Cooling rate



Cooling curve for Glen Dessary syenite (Scotland), based on distinct blocking temperatures for various minerals and isotopic systems (van Breemen et al. 1979).

Blocking temperatures

Mineral	Isotopic system	Closure T
Zircon	U – Pb	> 800 °C
Baddeleyite	U – Pb	> 800 °C
Monazite	U – Pb	≈ 700 °C
Titanite	U – Pb	≈ 600 °C
Garnet	U – Pb	> 550 °C
Garnet	Sm – Nd	> 550 °C
Amphibole	K – Ar	≈ 500 °C
Muscovite	Rb – Sr	≈ 500 °C
Plagioclase	Rb – Sr	≈ 450 °C
Muscovite	K – Ar	≈ 350 °C
Apatite	U – Pb	≈ 350 °C
Biotite	Rb – Sr	≈ 300 °C
Biotite	K – Ar	≈ 280 °C
K-feldspar	K – Ar	≈ 200 °C



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Web links

- Geochemistry 455 (W.M. White, Cornell University)
  http://www.geo.cornell.edu/geology/classes/geo455/Geo455.html
- Igneous and metamorphic geology
  (J. D. Winter, Whitman University)
  http://www.whitman.edu/geology/winter/JDW_PetClass.htm
- Isotopic Geology 656 (W.M. White, Cornell University)
  http://www.geo.cornell.edu/geology/classes/Geo656/656home.html
- Dickin – Radiogenic Isotopes Geology
  http://www.onafarawayday.com/Radiogenic/
- Flashed teaching resources in geology from the
  University of Tromsø, Norway
  http://ansatte.uit.no/kku000/webgeology/