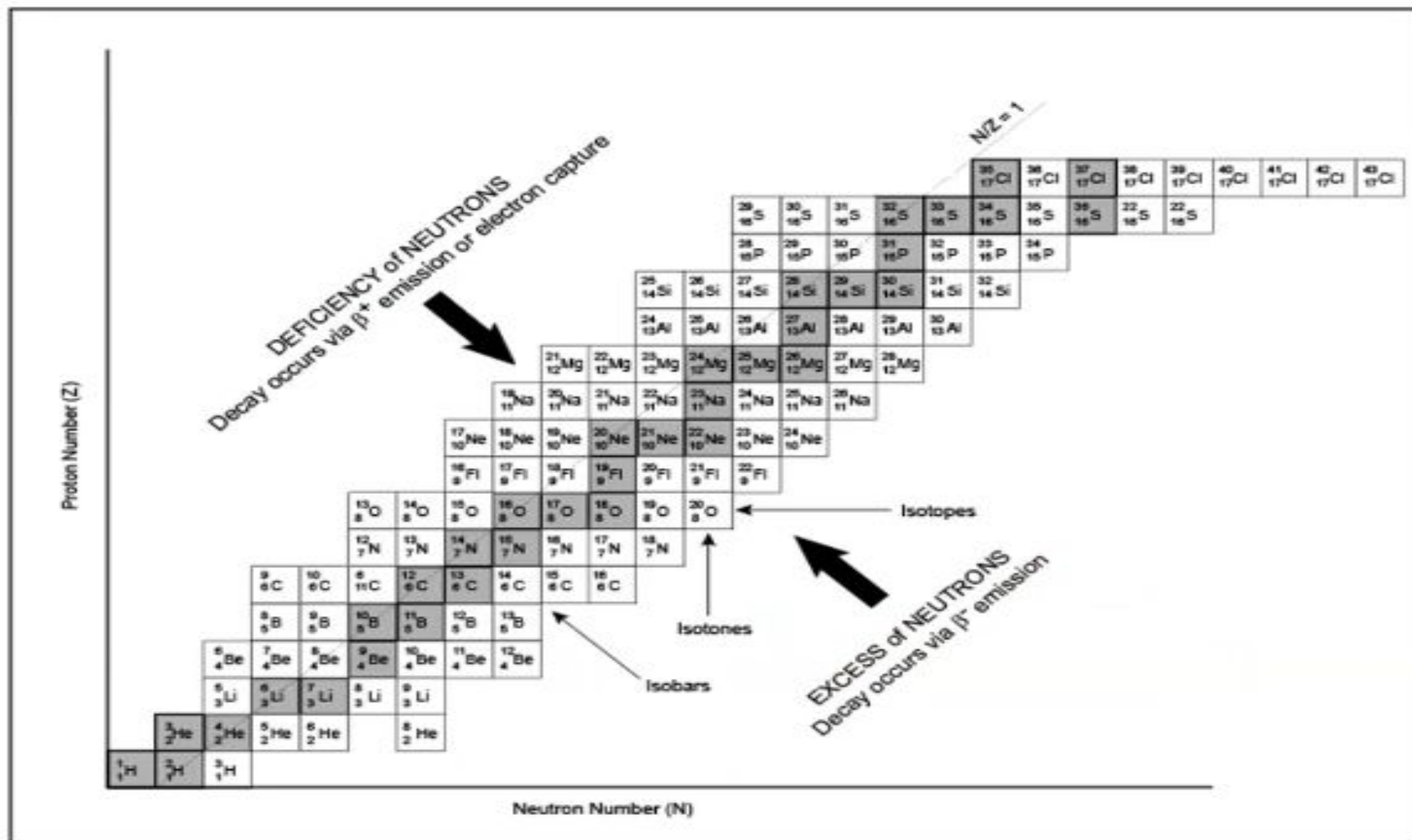


Stable versus Unstable Nuclides

- Not all combinations of N and Z result in stable nuclides.
- Some combinations result in stable configurations - *nuclides within the valley of β -stability*
 - Relatively few combinations
 - Generally $N \approx Z$
 - However, as A becomes larger, $N > Z$
- For some combinations of N+Z a nucleus forms but is unstable with half lives of $> 10^5$ yrs to $< 10^{-12}$ sec
- These unstable nuclides transform to stable nuclides through radioactive decay

Proton-rich or neutron-rich nuclides undergo decay



Radioactive Decay

- Nuclear decay follows the law of radioactive decay
- Radioactive decay has three characteristics:
 1. The decay rate is dependent only on the energy state of the nuclide
 2. The decay rate is independent of the history of the nucleus
 3. The decay rate is independent of pressure, temperature and chemical composition
- The timing of radioactive decay is impossible to predict but we can predict the probability of its decay in a given time interval

Radioactive Decay

- The probability of decay in some infinitesimally small time interval, **dt**, is **λdt** , where λ is the decay constant for the particular isotope
- The rate of decay among some number, N , of nuclides is therefore
 $dN / dt = -\lambda N$

The minus sign indicates that N decreases over time.

Decay rate

Radioactive decay rate proportional to number of atoms present

$$\frac{dN}{dt} = -\lambda N$$

N is the number of parent atoms in the sample
 λ is the decay constant (units t^{-1})

λN gives the activity (disintegrations/time)

Radioactive decay equation


Amount remaining as function of time:
if

$$\frac{dN}{dt} = -\lambda N$$

with

$$N_{(t=0)} = N_{(0)}$$

then

$$N_{(t)} = N_{(0)} e^{-\lambda t}$$


Number of daughter atoms produced:

$$D^* = N_0 - N$$

$$D^* = N_0 - N_0 e^{-\lambda t}$$

No. of stable daughter at any time t:

$$D^* = N_0 (1 - e^{-\lambda t})$$

In geological systems, what we measure is `N` and not `N_o` which we don't know

We relate the number of radiogenic daughter to the number of parent atoms remaining

$$D^* = N_o - N$$

$$D^* = N e^{\lambda t} - N$$

$$D^* = N (e^{\lambda t} - 1)$$

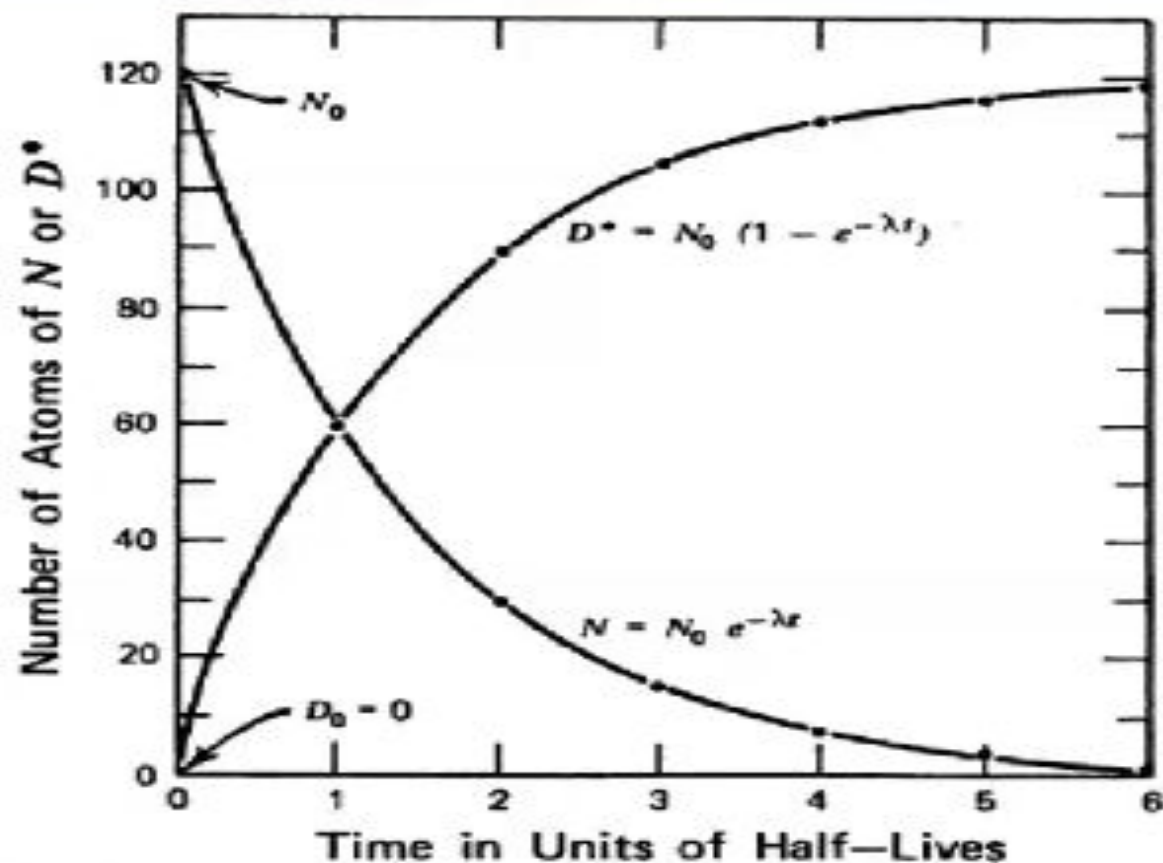


If there were some atoms of daughter present initially when the rock/mineral formed

$$D = D_o + D^*$$

$D = D_o + N (e^{\lambda t} - 1)$ Basic equation of geochronology

Radioactive parent decaying to stable daughter



ingrowth

decay

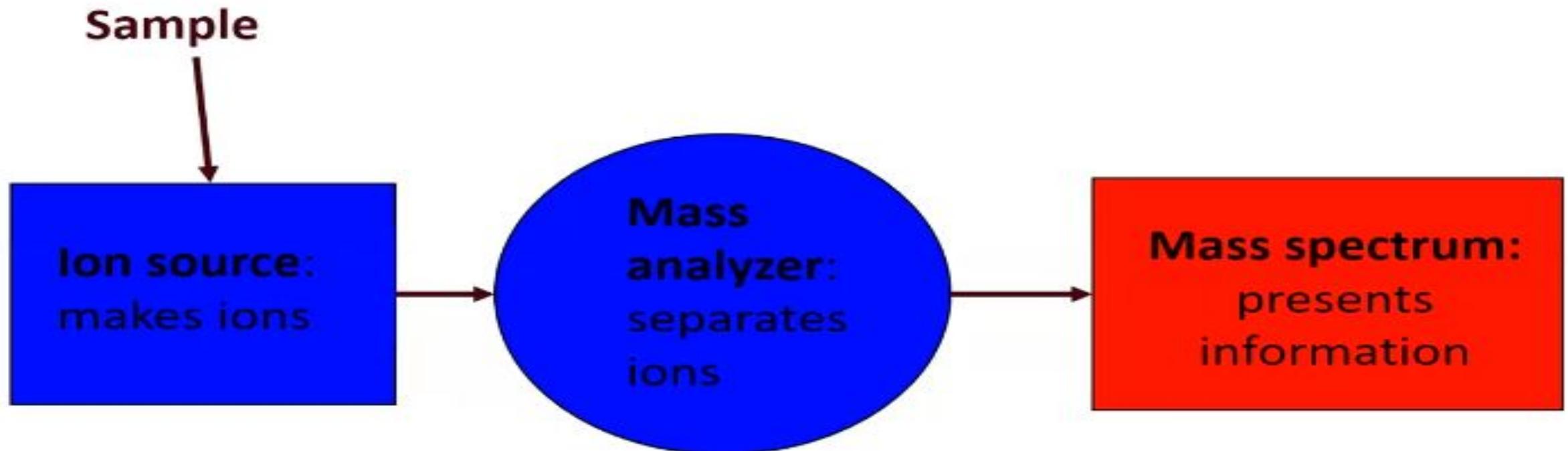
FIGURE 4.1 Decay of a hypothetical radionuclide (N) to a stable radiogenic daughter (D^*) as a function of time measured in units of half-lives. It can be seen that $N \rightarrow 0$ as $t \rightarrow \infty$, while $D^* \rightarrow N_0$ as $t \rightarrow \infty$.

Geologically Important Isotopes and their Decay Constants

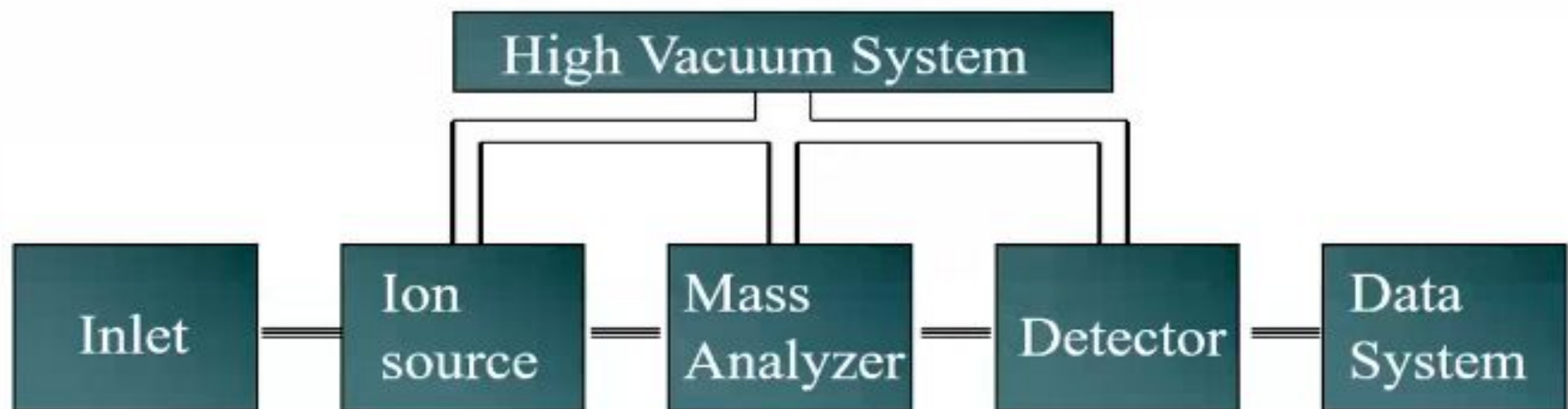
Parent	Decay Mode	λ	Half-life	Daughter	Ratio
^{40}K	β^+ e.c. β^-	$5.543 \times 10^{-10} \text{yr}^{-1}$	$1.28 \times 10^9 \text{yr}$	$^{40}\text{Ar}, ^{40}\text{Ca}$	$^{40}\text{Ar}/^{36}\text{Ar}$
^{87}Rb	β^-	$1.42 \times 10^{-11} \text{yr}^{-1}$	$4.8 \times 10^{10} \text{yr}$	^{87}Sr	$^{87}\text{Sr}/^{86}\text{Sr}$
^{138}La	β^-	$2.67 \times 10^{-12} \text{yr}^{-1}$	$2.59 \times 10^{11} \text{yr}$	$^{138}\text{Ce}, ^{138}\text{Ba}$	$^{138}\text{Ce}/^{142}\text{Ce}, ^{138}\text{Ce}/^{136}\text{Ce}$
^{147}Sm	α	$6.54 \times 10^{-12} \text{yr}^{-1}$	$1.06 \times 10^{11} \text{yr}$	^{143}Nd	$^{143}\text{Nd}/^{144}\text{Nd}$
^{176}Lu	β^-	$1.94 \times 10^{-11} \text{yr}^{-1}$	$3.6 \times 10^{10} \text{yr}$	^{176}Hf	$^{176}\text{Hf}/^{177}\text{Hf}$
^{187}Re	β^-	$1.64 \times 10^{-11} \text{yr}^{-1}$	$4.23 \times 10^{10} \text{yr}$	^{187}Os	$^{187}\text{Os}/^{188}\text{Os}, (^{187}\text{Os}/^{186}\text{Os})$
^{190}Pt	α	$1.54 \times 10^{-12} \text{yr}^{-1}$	$4.50 \times 10^{11} \text{yr}$	^{186}Os	$^{186}\text{Os}/^{188}\text{Os}$
^{232}Th	α	$4.948 \times 10^{-11} \text{yr}^{-1}$	$1.4 \times 10^{10} \text{yr}$	$^{208}\text{Pb}, ^4\text{He}$	$^{208}\text{Pb}/^{204}\text{Pb}, ^3\text{He}/^4\text{He}$
^{235}U	α	$9.849 \times 10^{-10} \text{yr}^{-1}$	$7.07 \times 10^8 \text{yr}$	$^{207}\text{Pb}, ^4\text{He}$	$^{207}\text{Pb}/^{204}\text{Pb}, ^3\text{He}/^4\text{He}$
^{238}U	alpha		1.55125×10^{10}	^{206}Pb	$^{206}\text{Pb}/^{204}\text{Pb}$

Mass spectrometry

Mass spectrometer is an instrument which is used to separate & measure charged atoms & molecules on the basis of their masses when they travel through an electric or magnetic field

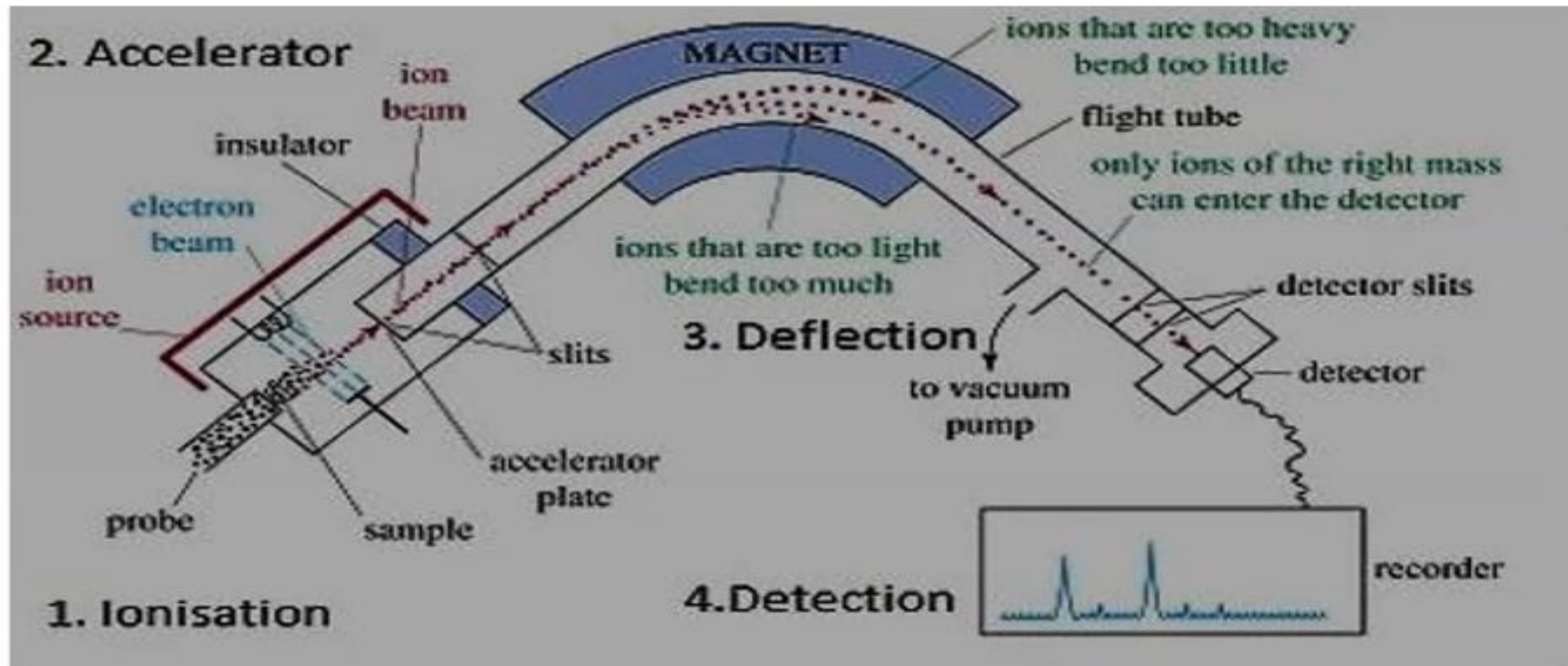


Mass Spectrometer Block Diagram

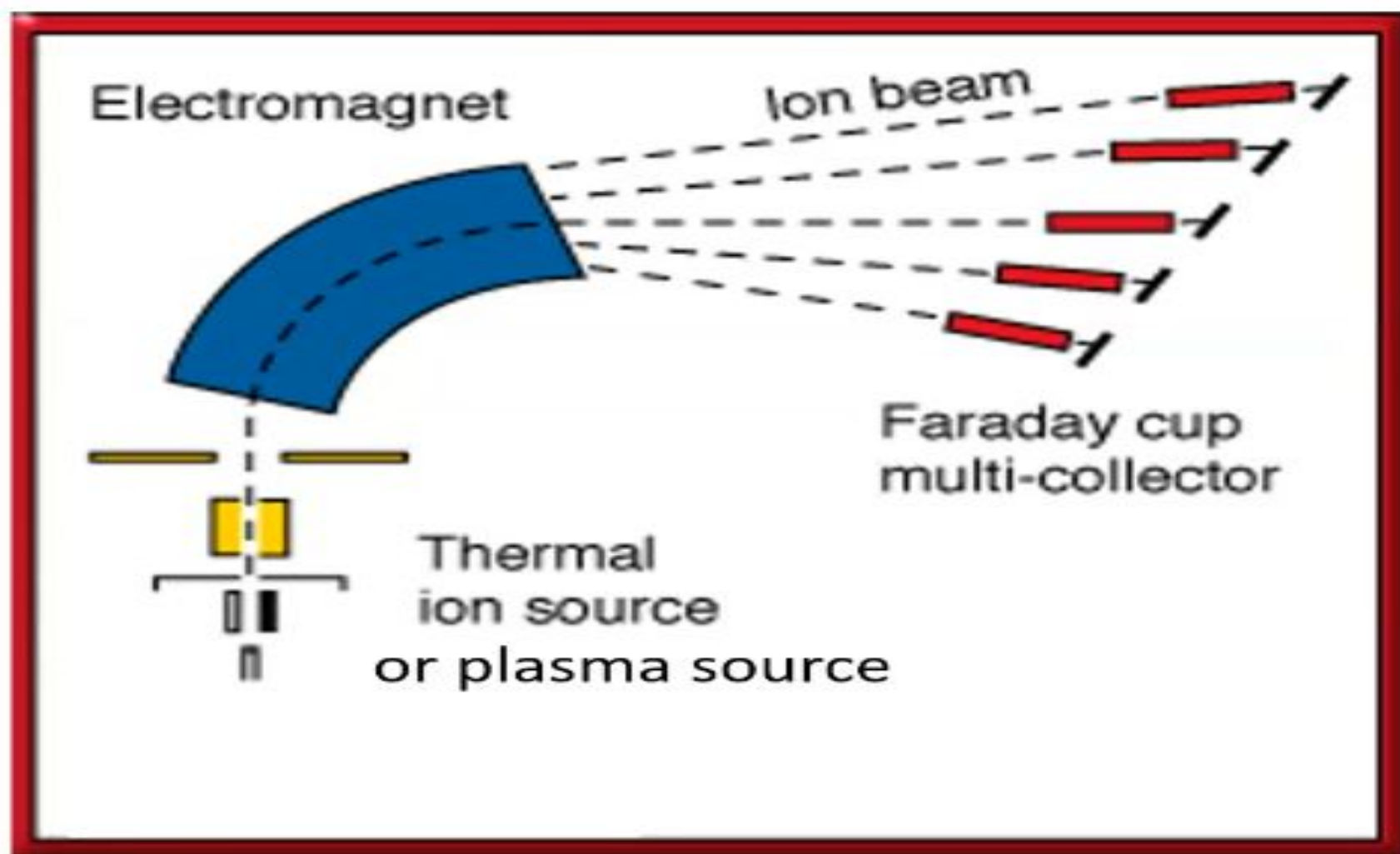


There are four key stages in the process for Mass Spectrometry

Ionization, Acceleration, Deflection, Detection



Thermal ionization/inductively coupled plasma multi collector mass spectrometer



Equation of motion of a charged particle in a magnetic sector mass spectrometer

$$E = eV = \frac{1}{2}mv^2 \text{ equation 1}$$

$$v = \sqrt{\frac{2eV}{m}}$$

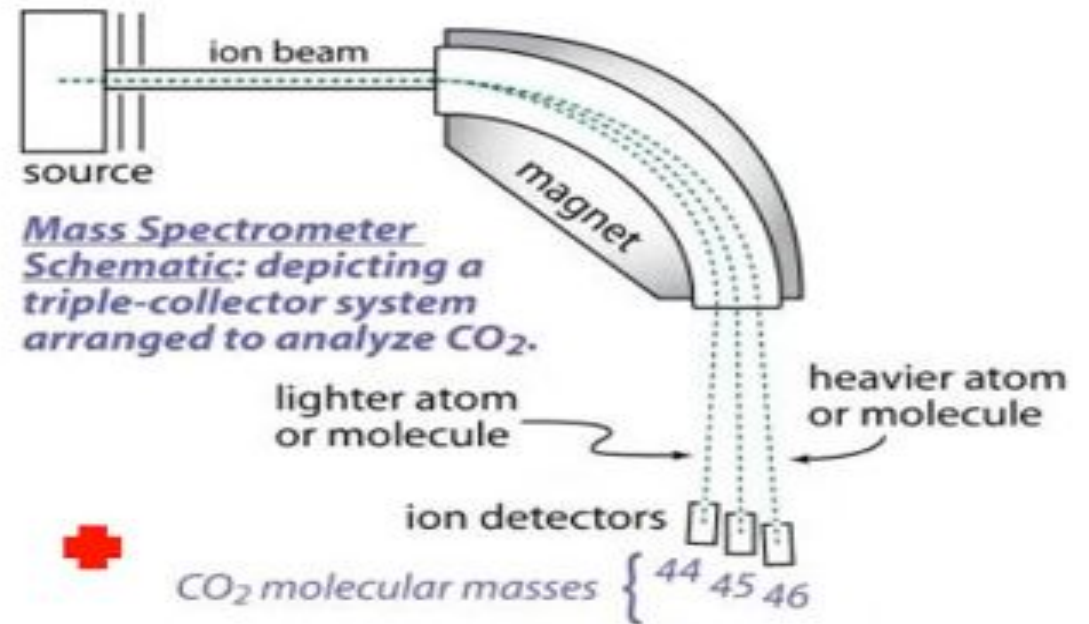
$$BeV = mv^2/r \text{ equation 2}$$

Eliminating v from equations (1) & (2)

$$2eV/m = B^2e^2r^2/m^2$$

$$m/e = B^2r^2/2V$$

$$r^2 = 2Vm/eB^2 \quad r = \frac{1}{B} \sqrt{\frac{2mV}{e}}$$



Rb-Sr System

Rubidium

- Rb is an alkali metal like Li, Na, K (group 1A)
- Ionic radii similar to K (Rb = 1.48 Å, K = 1.33 Å)
- Rb substitutes for K in all K—bearing minerals, such as muscovite, biotite, phlogopite, K — feldspar, clay minerals

Rb has two naturally occurring isotopes:

	$^{85}\text{Rb}_{37}$	$^{87}\text{Rb}_{37}$	$^{85}\text{Rb}/^{87}\text{Rb}$
Abundance (%)	72.1654	27.8346	2.59265
Mass (a.m.u.)	84.911785	86.909287	
Average atomic weight	85.46776		

^{87}Rb is radioactive and undergoes β^- decay to ^{87}Sr



Strontium

- alkaline earth element similar to Mg, Ca, Sr, Ba (group IIA)
- ionic radii slightly larger than that of Ca (Sr = 1.13 Å, Ca = 0.99 Å)
- replaces Ca in several minerals such as plagioclase, apatite, calcium carbonate

Sr has four naturally occurring isotopes:

	$^{84}\text{Sr}_{38}$	$^{86}\text{Sr}_{38}$	$^{87}\text{Sr}_{38}$	$^{88}\text{Sr}_{38}$	
Abundance	0.56	9.87	7.04	82.53	
Mass	83.913428	85.909273	86.90889	87.905625	
$^{88}\text{Sr}_{38}/^{86}\text{Sr}_{38} =$	8.37521	$^{84}\text{Sr}_{38}/^{86}\text{Sr}_{38} =$	0.056584	$^{87}\text{Sr}_{38}/^{86}\text{Sr}_{38} =$	0.7....

- ^{86}Sr is a stable isotope, and not created by breakdown of any other parent-used as a reference isotope in the denominator of isotope ratios

Average Rb and Sr concentrations in rocks

Rock	Rb (ppm)	Sr (ppm)	Rb/Sr
Ultra basic	0.2	1.0	low
Basaltic	30	465	low
Syenite	110	200	high
Granite	150	300	high
Sandstone	60	20	high
Clay	110	180	high
Shale	140	300	high

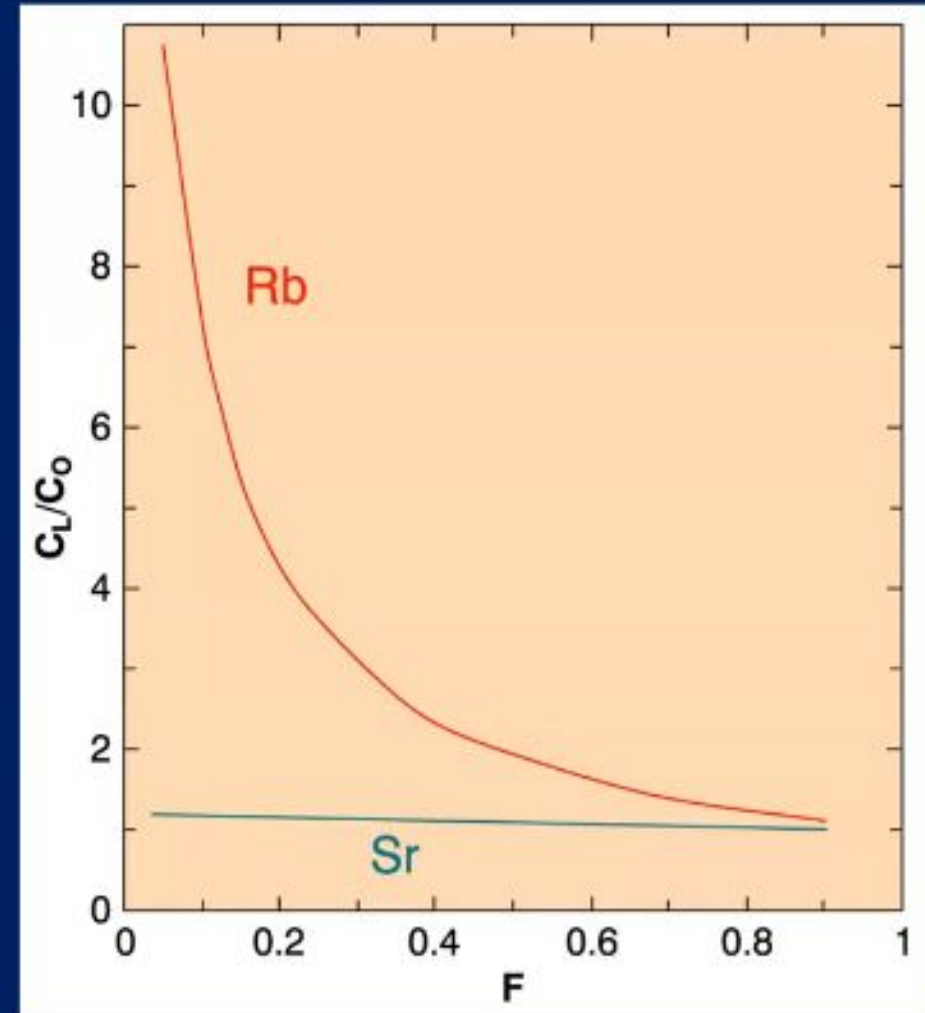
Behavior of Rb and Sr during mantle partial melting and magmatic differentiation

- Both Rb and Sr are incompatible elements in mantle mineral
- Rb is more incompatible than Sr

- During partial melting of mantle, Rb is concentrated more in the melt phase than Sr



- During fractional crystallization of magma, Sr is concentrated in plagioclase whereas Rb remains in the melt
- Consequently the Rb/Sr ratio of residual magma may increase gradually



Dating Rb-bearing minerals in igneous rocks

$$^{87}\text{Sr} = ^{87}\text{Sr}_i + ^{87}\text{Rb} (e^{\lambda t} - 1)$$

- Because it is easier to measure ratios of isotopes in a mass spectrometer, we can divide all terms by a stable isotope of Sr

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

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

- In order to solve for t , one has to know the initial isotope composition. This is an unknown. One can assume an initial and calculate a date. This will be a **model age**
- Alternatively use the isochron technique**

Isochron technique

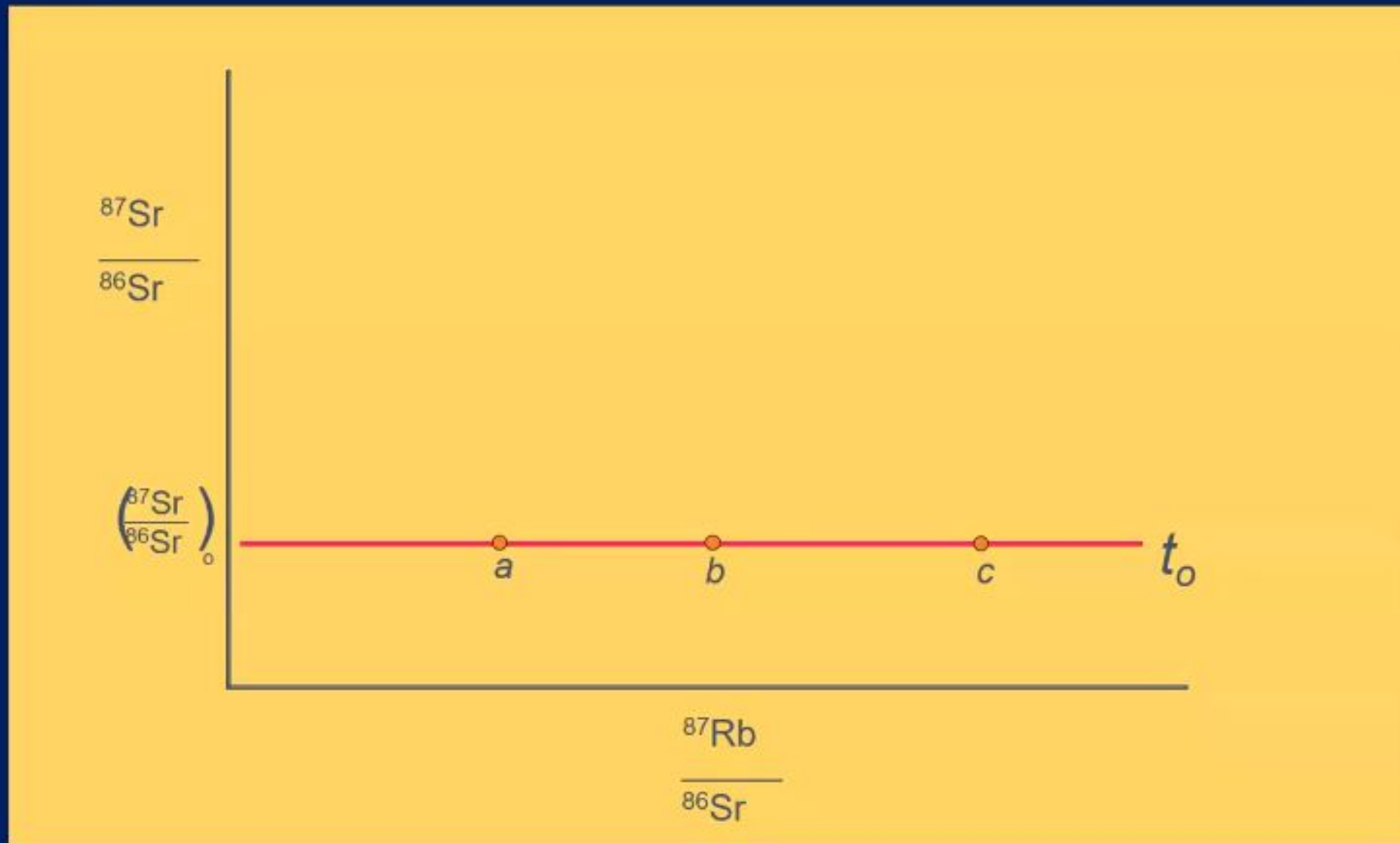
In co-ordinates of $^{87}\text{Sr}/^{86}\text{Sr}$ (Y) and $^{87}\text{Rb}/^{86}\text{Sr}$ (X), the decay equation is an equation of a straight line

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

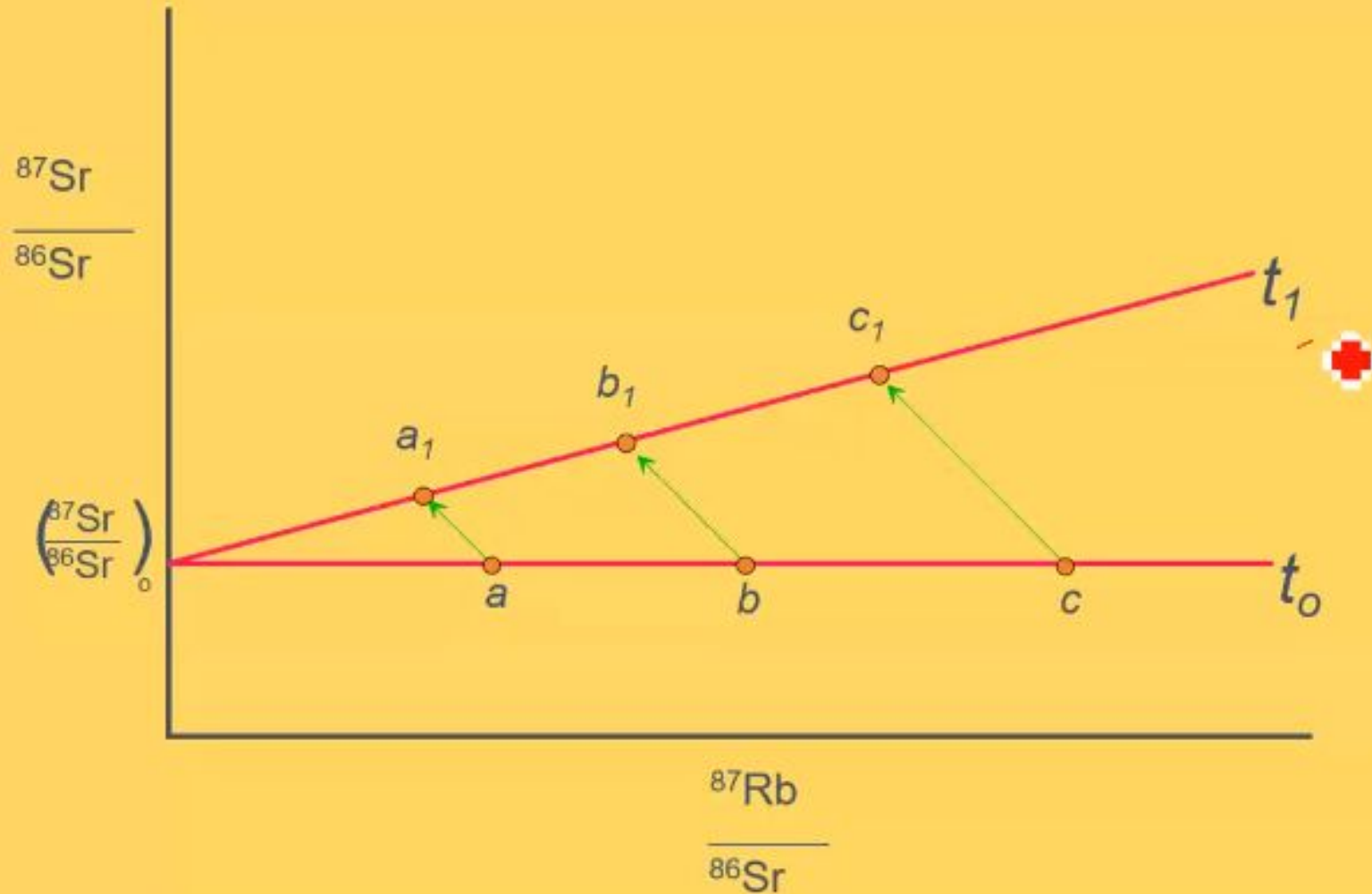
$$Y = C + X m$$

- All rock specimens of a co-magmatic and coeval suite will plot as points on a straight line. This line is called an **ISOCHRON**
- This is because all points on that line represent system/rock having the same age and the same initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio

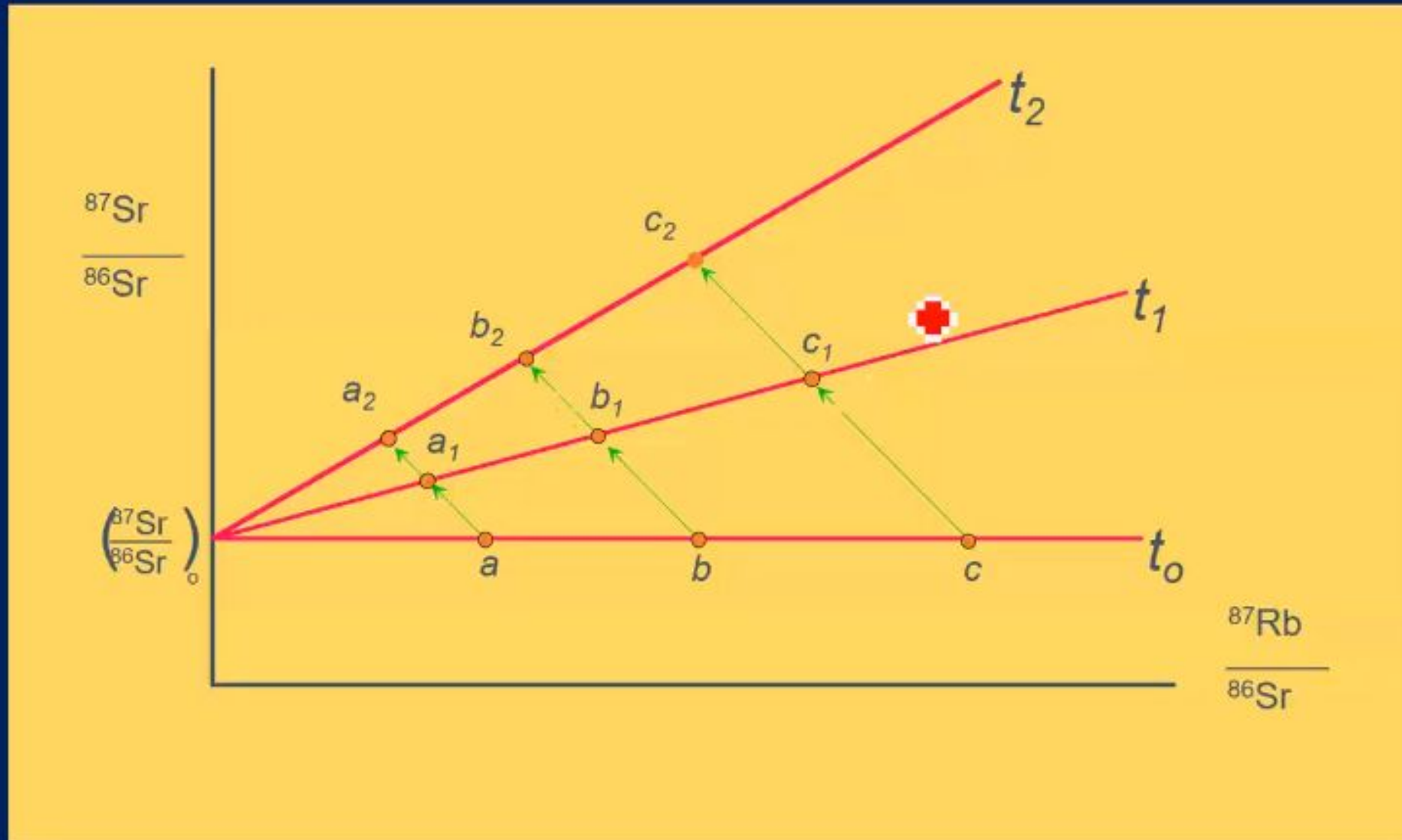
Begin with 3 rocks plotting at a, b, c, at time t_0



After some time increment ($t_0 \rightarrow t_1$) each sample loses some ^{87}Rb and gains an equivalent amount of ^{87}Sr



At time t_2 each rock system has evolved \rightarrow new line
Again still linear and steeper line



Isochron technique gives two important pieces of information:

1. The age of the rocks from the slope of the isochron
2. $(^{87}\text{Sr}/^{86}\text{Sr})_0$ = the initial value of $^{87}\text{Sr}/^{86}\text{Sr}$

$$m = (e^{\lambda t} - 1)$$

$$t = 1/\lambda * \ln(1+m)$$

The initial isotope ratio is used as petrogenetic indicator

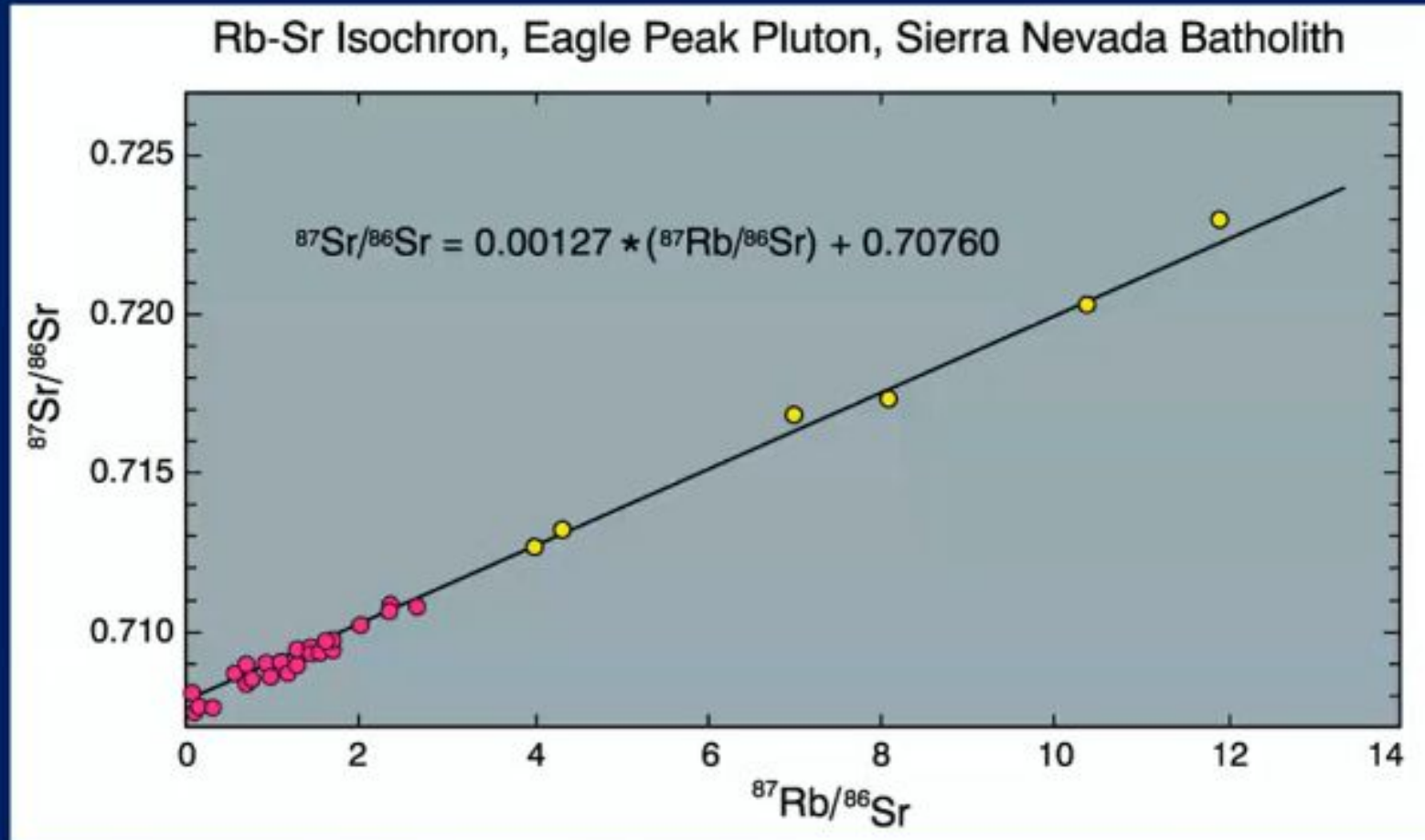
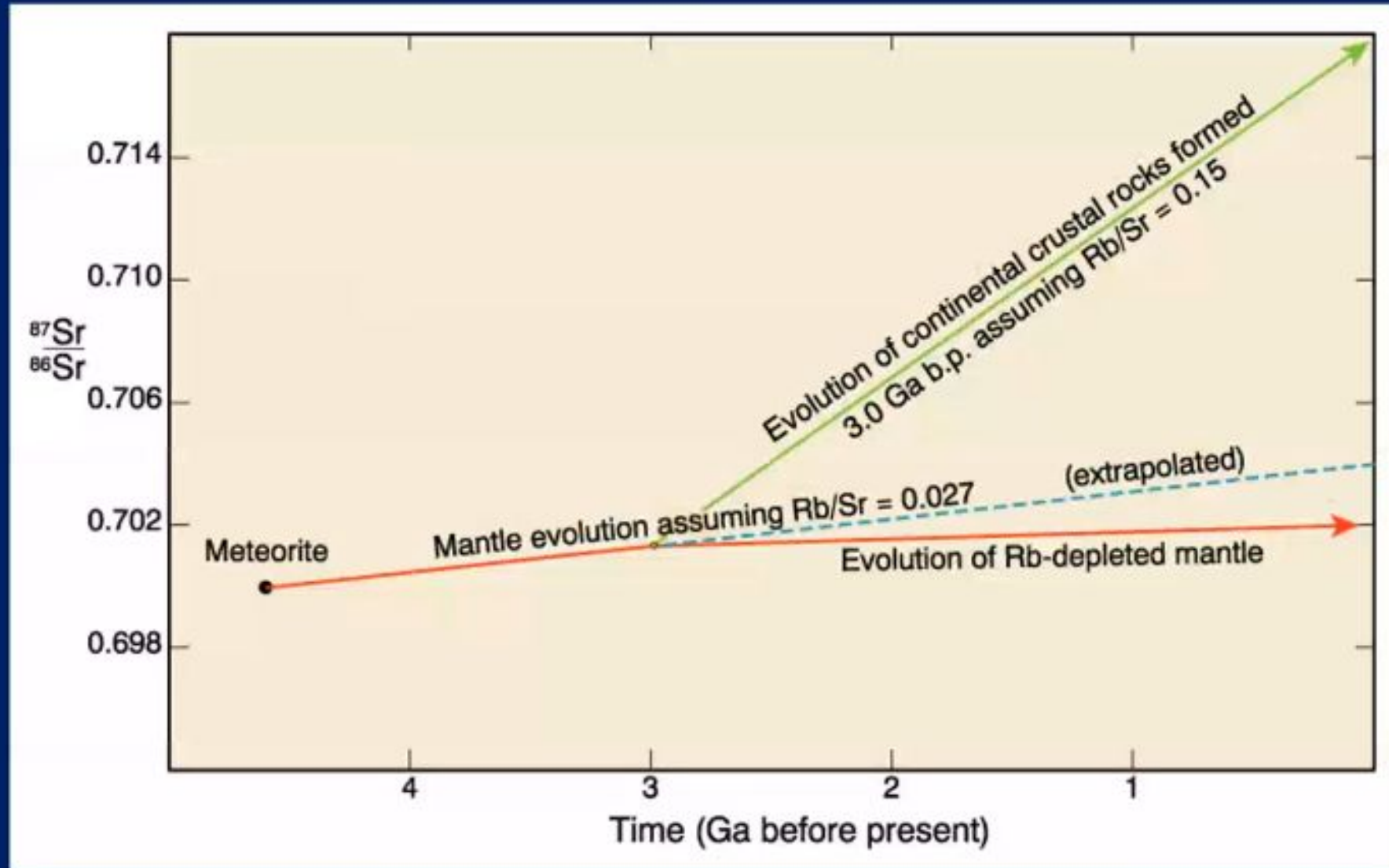


Figure 9-9. Rb-Sr isochron for the Eagle Peak Pluton, central Sierra Nevada Batholith, California, USA. Filled circles are whole-rock analyses; open circles are hornblende separates. The regression equation for the data is also given. After Hill et al. (1988), Amer. J. Sci., 286-A, 213-241.

Sr isotope evolution of mantle and crustal reservoirs



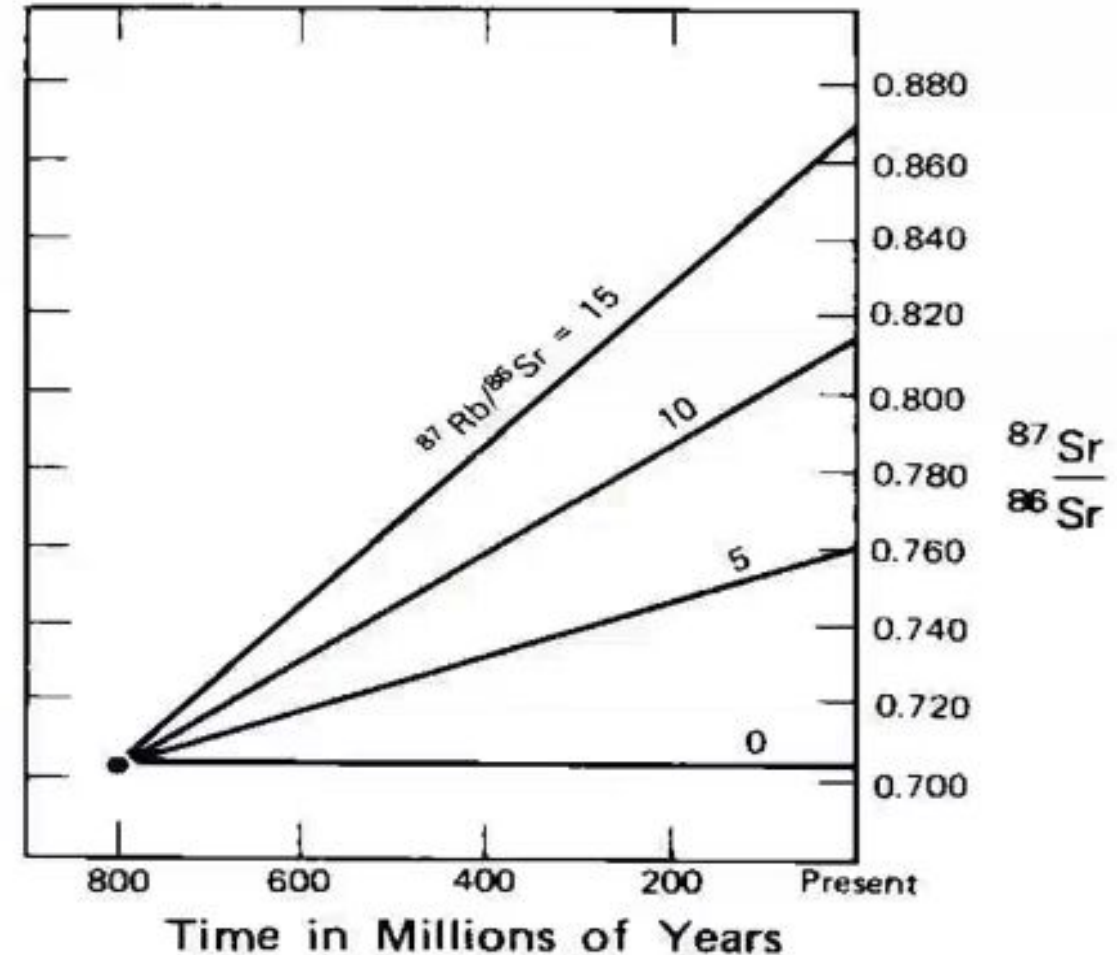
Isotope evolution diagram

Undertaking power series expansion of $e^{\lambda t}$ and neglecting higher order terms, the decay equation can be approximated to:

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

$$Y = C + MX$$

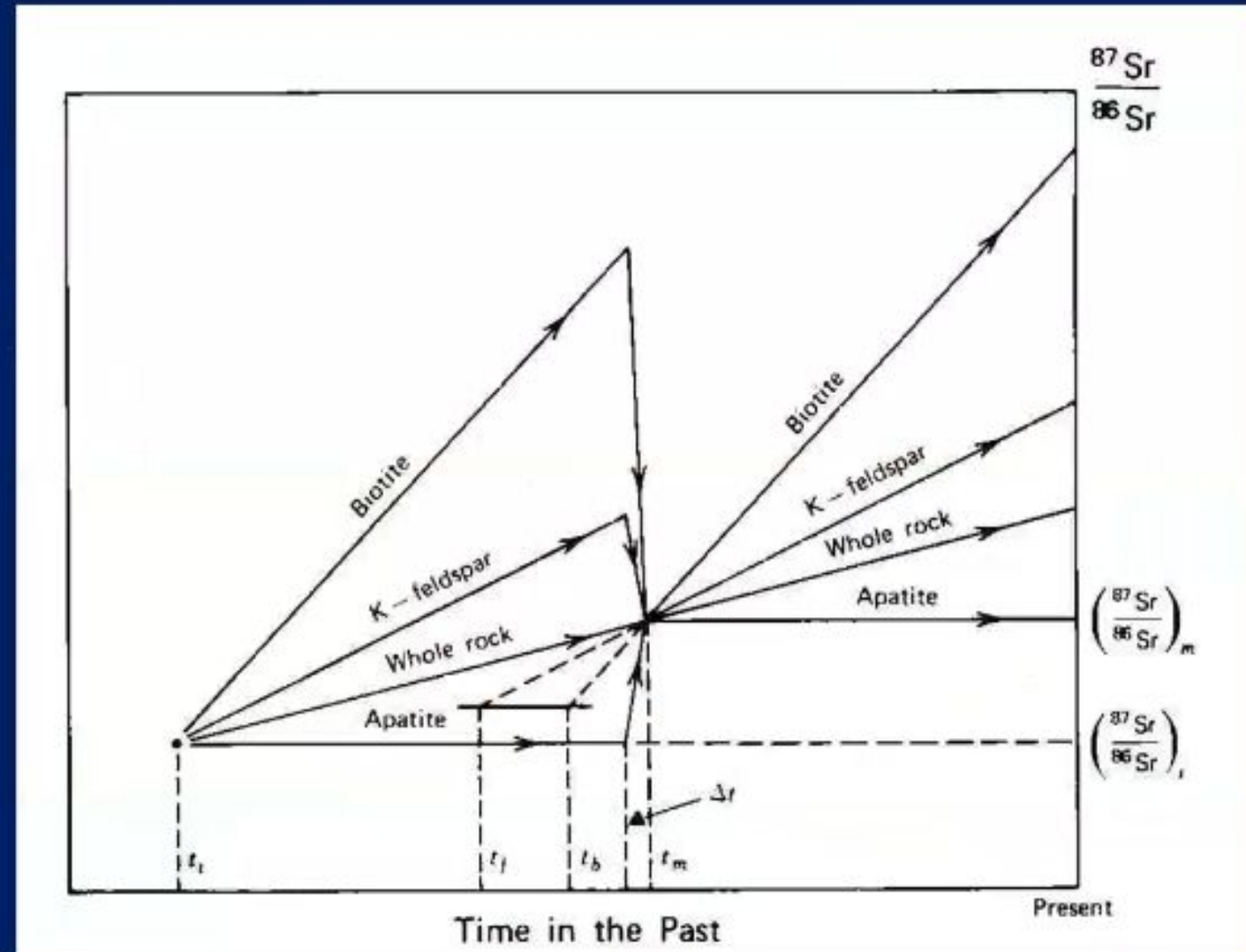
One can construct isotope evolution diagram, i.e. isotope ratio vs. time where the slope of the line depends on the Rb/Sr ratio of the mineral or rock



Dating metamorphism using high Rb-Sr bearing minerals

Assumptions

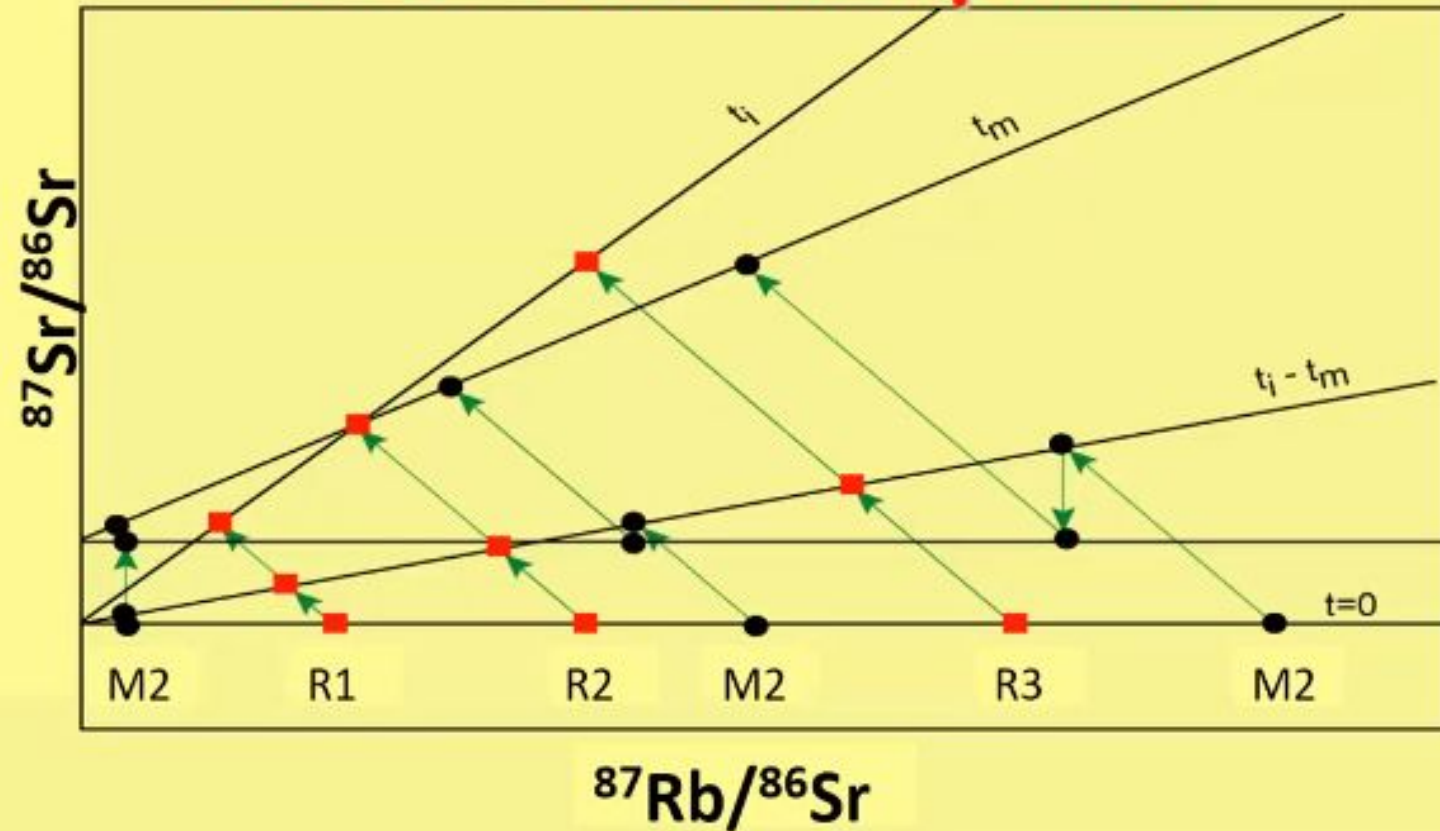
- Rock remained closed on a whole rock scale
- Radiogenic Sr was exchanged and homogenized during the metamorphism
- Rb and Sr concentrations of minerals remained unchanged during the metamorphism



Dating both igneous crystallization and metamorphism

- Using whole rocks and minerals

Rb-Sr metamorphism



Sm-Nd isotope system

Sm-Nd geochemistry

Both Sm and Nd are LREE

- Incompatible elements fractionate → melts
 - Nd has lower Z → larger → liquids > does Sm
-
- + 3 charge, decreasing ionic radii with increasing atomic number.
 - REE found in many accessory minerals in rocks-**apatite, zircon, allanite, monazite**
 - $\text{Nd}^{3+} \rightarrow 1.08 \text{ \AA}$ $\text{Sm}^{3+} \rightarrow 1.04 \text{ \AA}$
 - Both incompatible elements
 - Concentrations of both elements increase with increasing differentiations
 - Because Sm^{3+} is slightly smaller, it is a little more compatible than Nd.
 - Sm / Nd ratio decreases with differentiation

7	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
	(132.91)	(137.33)	138.91	178.49	180.95	183.84	186.21	190.23	192.22	195.08	196.97	200.59	204.38	207.2	208.98	(209)	(210)	(222)
	Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Uun	Uuu	Uub						
	(223)	(226)	(227)	(261.1)	(262.1)	(263.1)	(262.1)	(265.1)	(266.1)	(269)	(272)	(277)						

Lanthanide Series	58	59	60	61	62	63	64	65	66	67	68	69	70	71
	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
	140.12	140.91	144.24	(144.9)	150.36	151.97	157.25	158.93	162.5	164.93	167.26	168.93	173.04	174.97
	80	81	82	83	84	85	86	87	88	89	90	91	92	93

Sm-Nd fractionation during partial melting of mantle

Partial melt



lower Sm/Nd



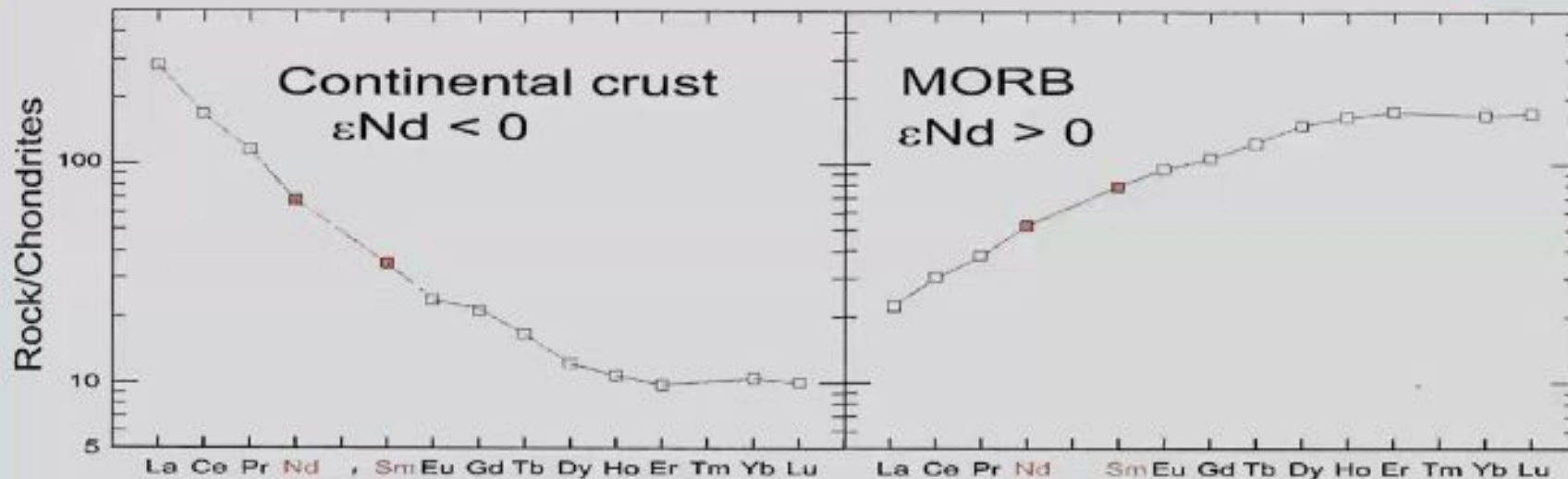
Mantle residue



Higher Sm/Nd

Nd is slightly more incompatible during mantle melting than Sm

Sm will be enriched in “depleted” sources (i.e. MORB) (opposite to Rb/Sr system, whereas Nd is enriched in continents)



Sm-Nd geochemistry

Average concentration of Sm & Nd in common terrestrial rocks and minerals

minerals

minerals	Sm(ppm)	Nd(ppm)	Sm/Nd
Olivine	0.07	0.36	0.19
Pyroxene	3.34	9.09	0.367
Amphibole	6.03	17.3	0.347
Biotite	37	171.5	0.215
Plagioclase	0.541	1.85	0.292

Volcanic rocks

rocks	Sm(ppm)	Nd(ppm)	Sm/Nd
Komatite	1.14	3.59	0.317
Alkali basalt	8.07	41.5	0.194
Andesites	3.90	20.6	0.189
Rhyolite	4.65	21.6	0.215

Sm-Nd isotope system

Isotopes of Nd

Isotope	¹⁴² Nd	¹⁴³ Nd	¹⁴⁴ Nd	¹⁴⁵ Nd	¹⁴⁶ Nd	¹⁴⁸ Nd	¹⁵⁰ Nd
Exact mass	141.908	142.909	143.910	144.913	145.913	147.917	149.921
Ratio to ¹⁴⁴ Nd	1.141854	0.513101	1.0	0.348416	0.7219	0.241572	0.236404

Isotopes of Sm

¹⁴²Sm, ¹⁴⁴Sm, ¹⁴⁶Sm, ¹⁴⁷Sm, ¹⁴⁹Sm, ¹⁵⁰Sm, ¹⁵²Sm, ¹⁵⁴Sm

Average atomic weight = 150.366

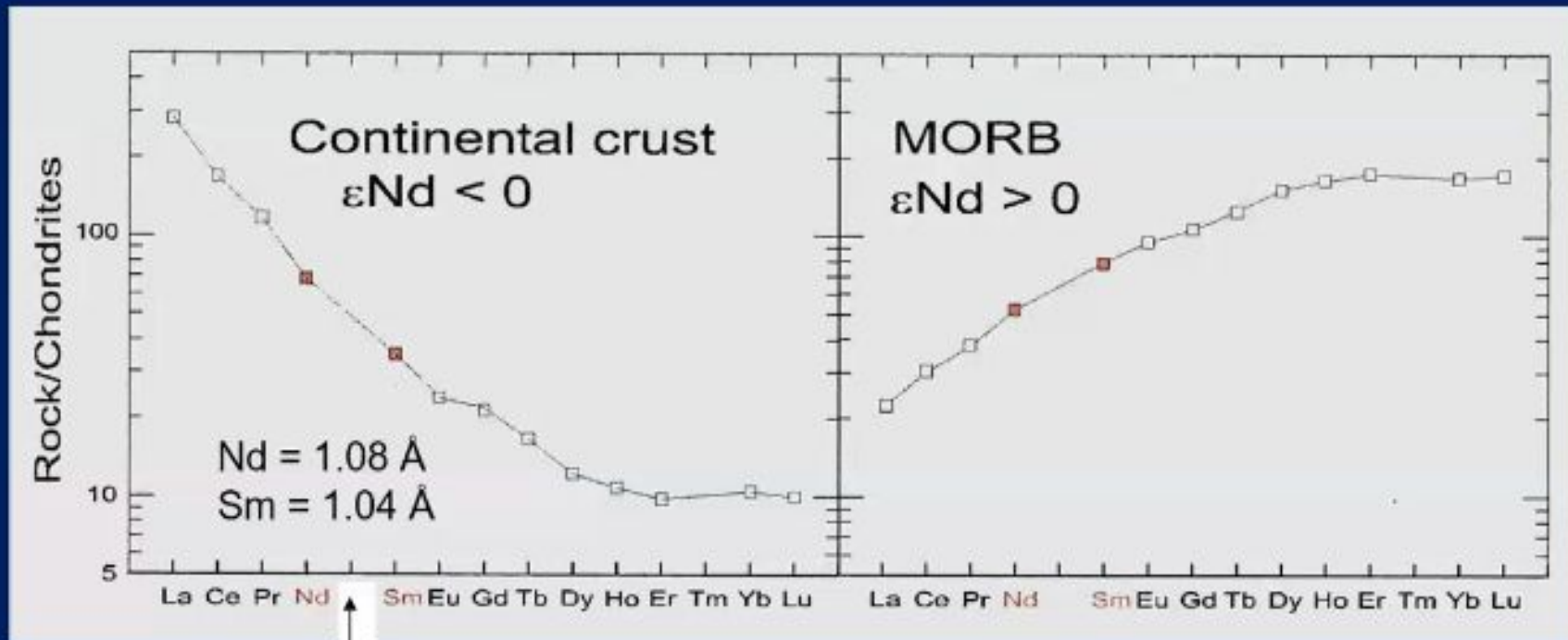
¹⁴⁷Sm → ¹⁴³Nd by alpha decay

$$\lambda = 6.54 \times 10^{-13} \text{ a}^{-1} \text{ (half life 106 Ga)}$$

▣ Decay equation derived by reference to the **non-radiogenic** ¹⁴⁴Nd

$$\square \text{ } ^{143}\text{Nd}/^{144}\text{Nd} = (^{143}\text{Nd}/^{144}\text{Nd})_0 + (^{147}\text{Sm}/^{144}\text{Nd})(e^{\lambda t} - 1)$$

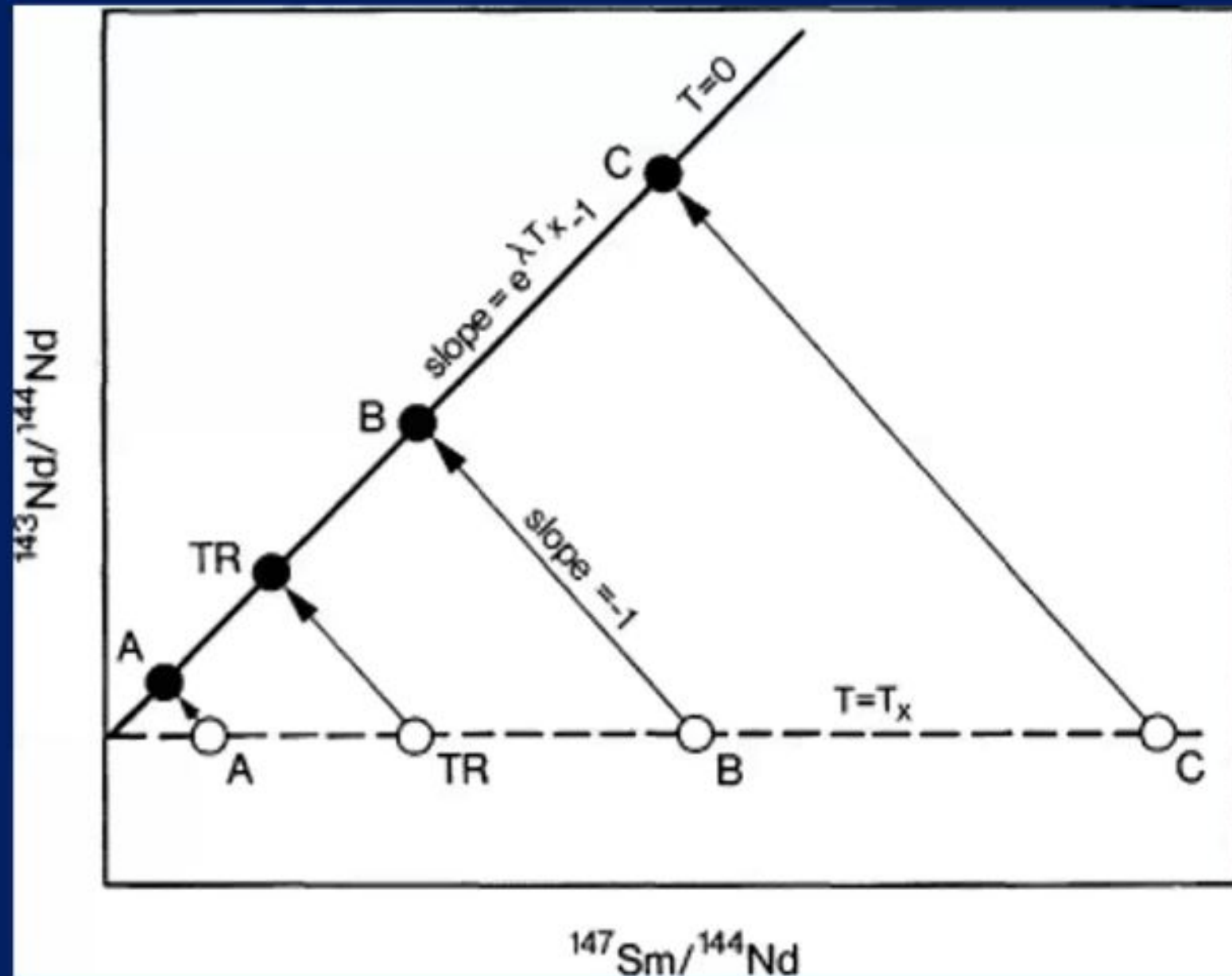
Sm-Nd decay



High **Sm/Nd** rocks produce more ^{143}Nd Low **Sm/Nd**
rocks produce less ^{143}Nd

Although the difference is small, $^{143}\text{Nd}/^{144}\text{Nd}$ increases faster in the mantle than in the crust. Thus, mantle-derived rocks have higher $(^{143}\text{Nd}/^{144}\text{Nd})_0$ than crustal rocks.

Sm-Nd isochron



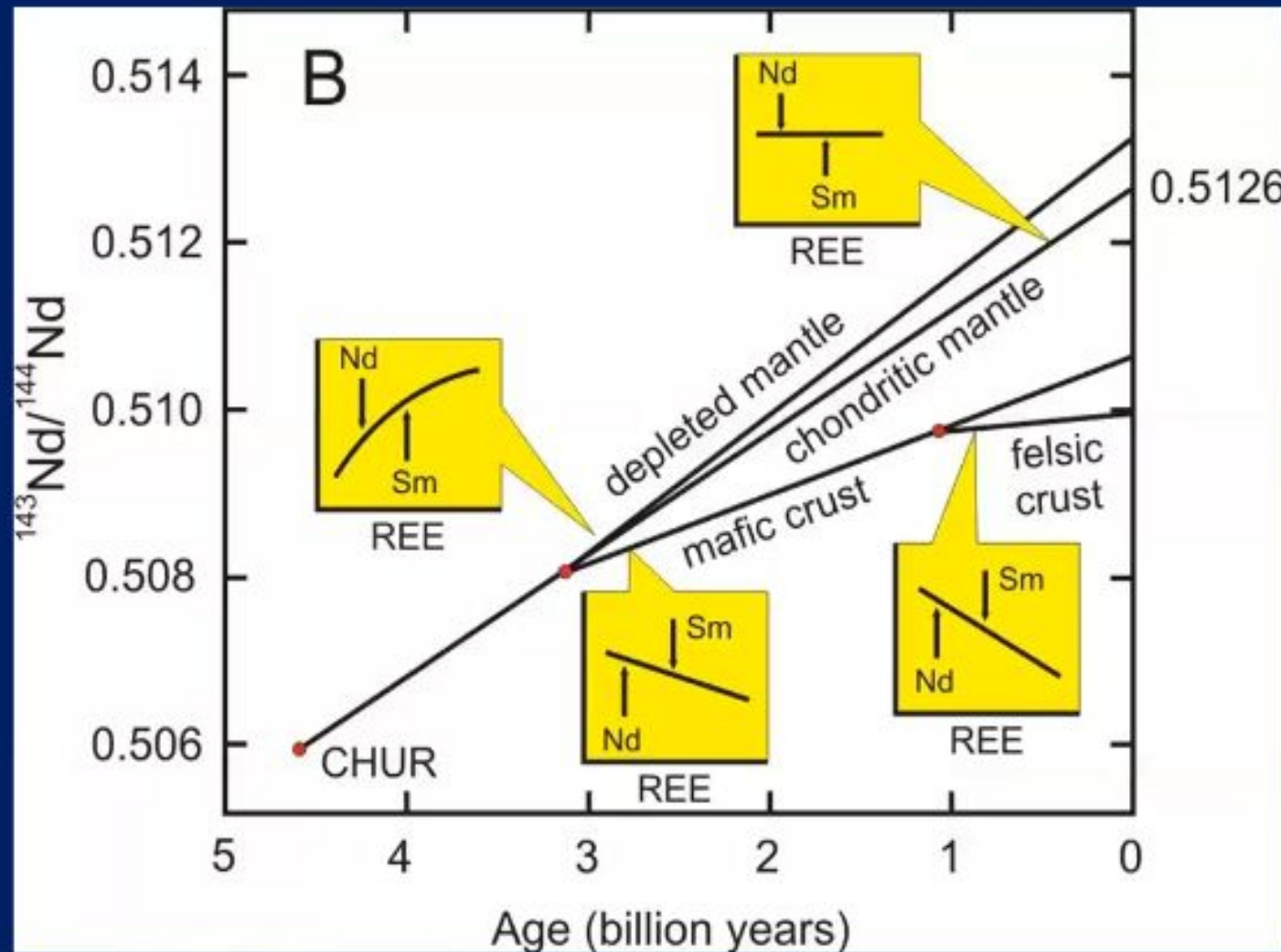
Isochron technique similar to that of Rb-Sr system

Relatively smaller variations in Sm/Nd ratios in natural rocks

Therefore difficulty in obtaining a wide range of Sm/Nd ratios from a single rock body

Suitable for dating minerals such as garnet and clinopyroxene

The evolution of Nd isotopes with time in the mantle, the continental crust and the bulk Earth (CHUR)



Isotopic evolution of Nd in the Earth is described in terms of model called **CHUR**

This model assumes that terrestrial Nd has evolved in a uniform reservoir whose Sm/Nd ratio & initial $^{143}\text{Nd}/^{144}\text{Nd}$ is equal to that of chondritic meteorites

CHUR today

$^{143}\text{Nd}/^{144}\text{Nd}=0.512638$

$^{147}\text{Sm}/^{144}\text{Nd}=0.1967$

Epsilon notation

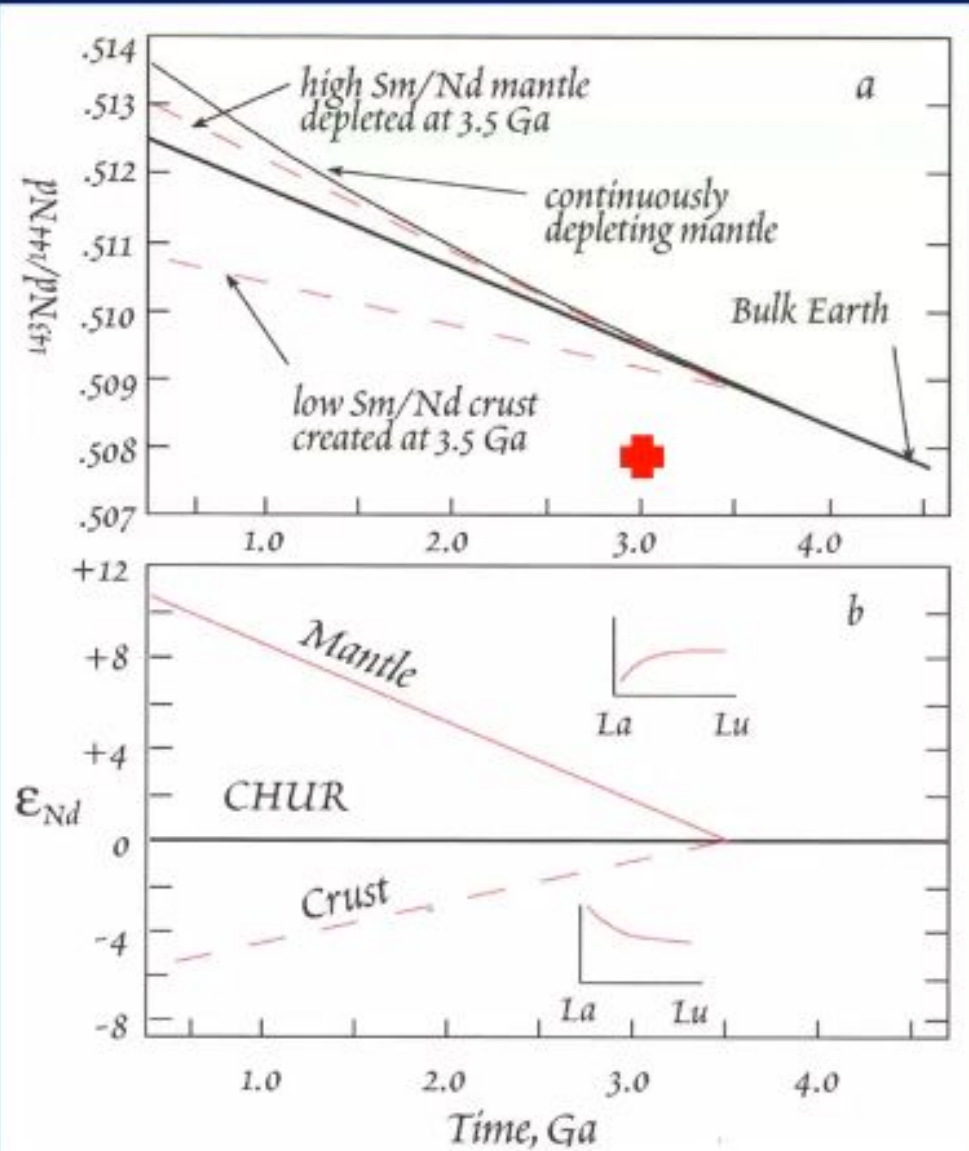
$$\epsilon_{Nd,CHUR} = \left[\frac{\left({}^{143}Nd / {}^{144}Nd \right)_{sample}}{\left({}^{143}Nd / {}^{144}Nd \right)_{CHUR}} - 1 \right] \times 10^4$$

The mantle has a higher $^{147}Sm/^{144}Nd$ ratio than CHUR, so the mantle has been evolving values of $^{143}Nd/^{144}Nd$ greater than CHUR with time, so

$\epsilon_{Nd,CHUR} > 1$ for mantle

The crust has a lower $^{147}Sm/^{144}Nd$ ratio than CHUR, so the crust has been evolving values of $^{143}Nd/^{144}Nd$ less than CHUR with time, so **$\epsilon_{Nd,CHUR} < 1$ for crust**

The evolution of Nd isotopes with time in the mantle, the continental crust and the bulk Earth (CHUR)



$$\epsilon_{\text{Nd,CHUR}} = \frac{T \left(\frac{^{143}\text{Nd}}{^{144}\text{Nd}} \right)_{\text{sample}}}{\left[\left(\frac{^{143}\text{Nd}}{^{144}\text{Nd}} \right)_{\text{CHUR}} \right]} - 1 \times 10^4$$

Nd model ages

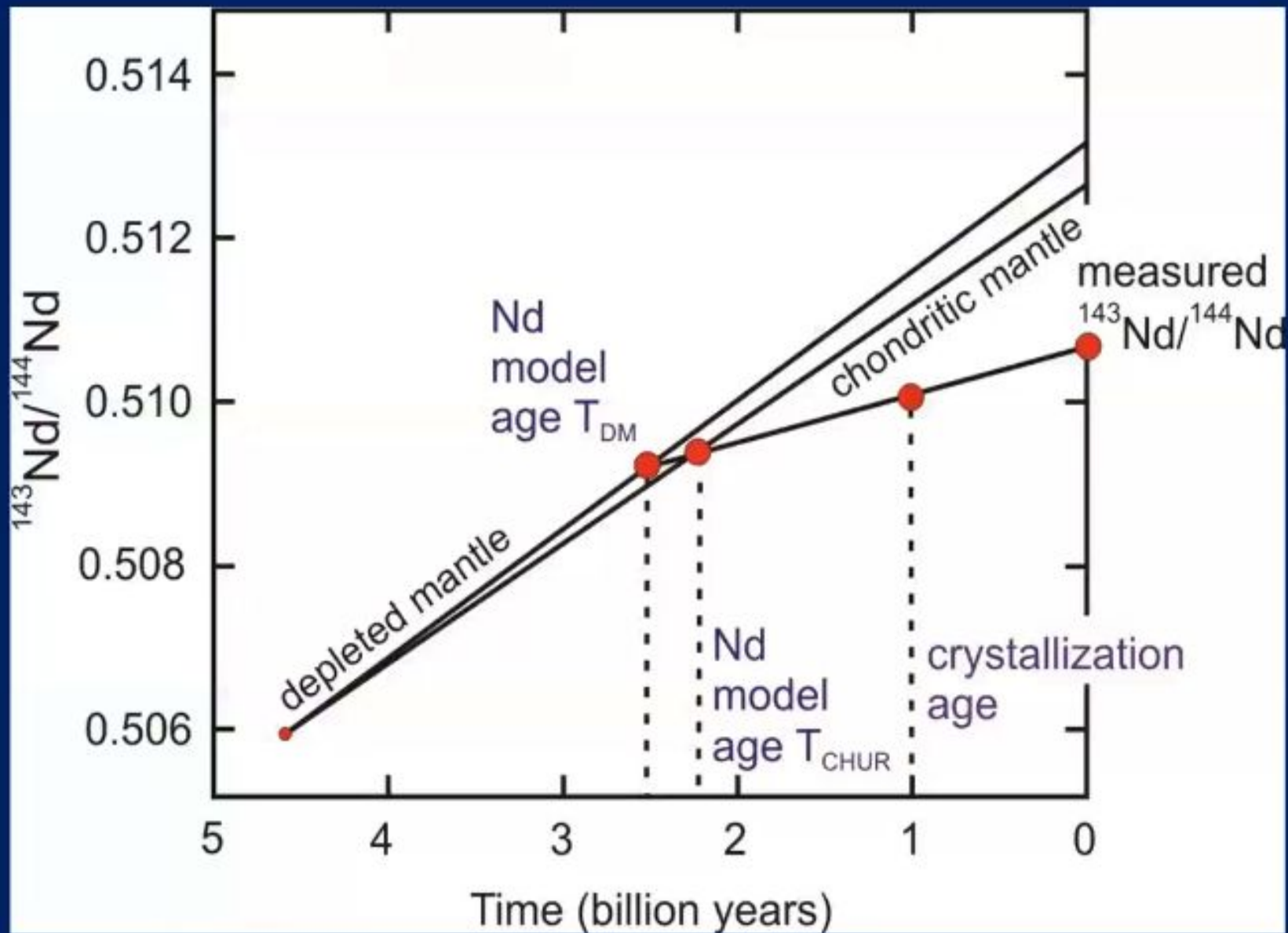
Model age - a measure of the length of time a sample has been separated from the mantle from which it was originally derived

Model ages can be calculated for an individual rock from a single pair of Sm-Nd isotopic ratios

The basis of all such model ages is an assumption about the isotopic composition of the mantle source region from which the samples were originally derived

Care must be exercised in their interpretation

Nd model ages



Nd model ages

$$\frac{{}^{143}\text{Nd}}{{}^{144}\text{Nd}}_{\text{sample}} = \frac{{}^{143}\text{Nd}}{{}^{144}\text{Nd}}_{\text{initial}} + \frac{{}^{147}\text{Sm}}{{}^{144}\text{Nd}}_{\text{sample}} \times (e^{\lambda t} - 1)$$

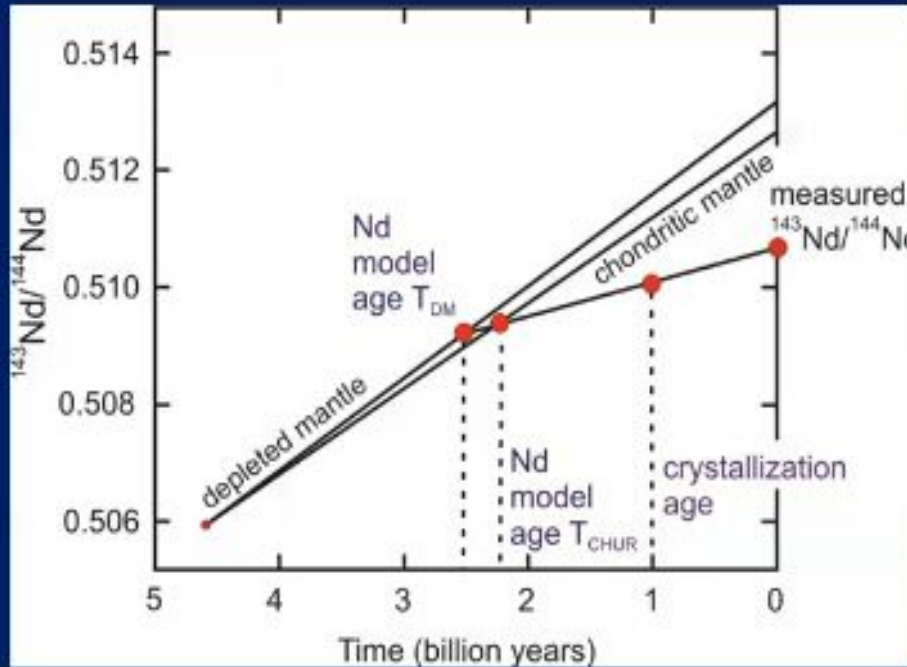
$$\frac{{}^{143}\text{Nd}}{{}^{144}\text{Nd}}_{\text{CHUR}} = \frac{{}^{143}\text{Nd}}{{}^{144}\text{Nd}}_{\text{initial}} + \frac{{}^{147}\text{Sm}}{{}^{144}\text{Nd}}_{\text{CHUR}} \times (e^{\lambda t} - 1)$$

$$\frac{{}^{143}\text{Nd}}{{}^{144}\text{Nd}}_{\text{sample}} - \frac{{}^{143}\text{Nd}}{{}^{144}\text{Nd}}_{\text{CHUR}} = \frac{{}^{147}\text{Sm}}{{}^{144}\text{Nd}}_{\text{sample}} - \frac{{}^{147}\text{Sm}}{{}^{144}\text{Nd}}_{\text{CHUR}} \times (e^{\lambda t} - 1)$$

$$(e^{\lambda t} - 1) = \frac{({}^{143}\text{Nd} / {}^{144}\text{Nd})_{\text{sample}} - ({}^{143}\text{Nd} / {}^{144}\text{Nd})_{\text{CHUR}}}{({}^{147}\text{Sm} / {}^{144}\text{Nd})_{\text{sample}} - ({}^{147}\text{Sm} / {}^{144}\text{Nd})_{\text{CHUR}}}$$

$$T_{\text{CHUR}} = \frac{1}{\lambda} \ln \frac{({}^{143}\text{Nd} / {}^{144}\text{Nd})_{\text{sample}} - ({}^{143}\text{Nd} / {}^{144}\text{Nd})_{\text{CHUR}}}{({}^{147}\text{Sm} / {}^{144}\text{Nd})_{\text{sample}} - ({}^{147}\text{Sm} / {}^{144}\text{Nd})_{\text{CHUR}}} + 1$$

Nd model ages

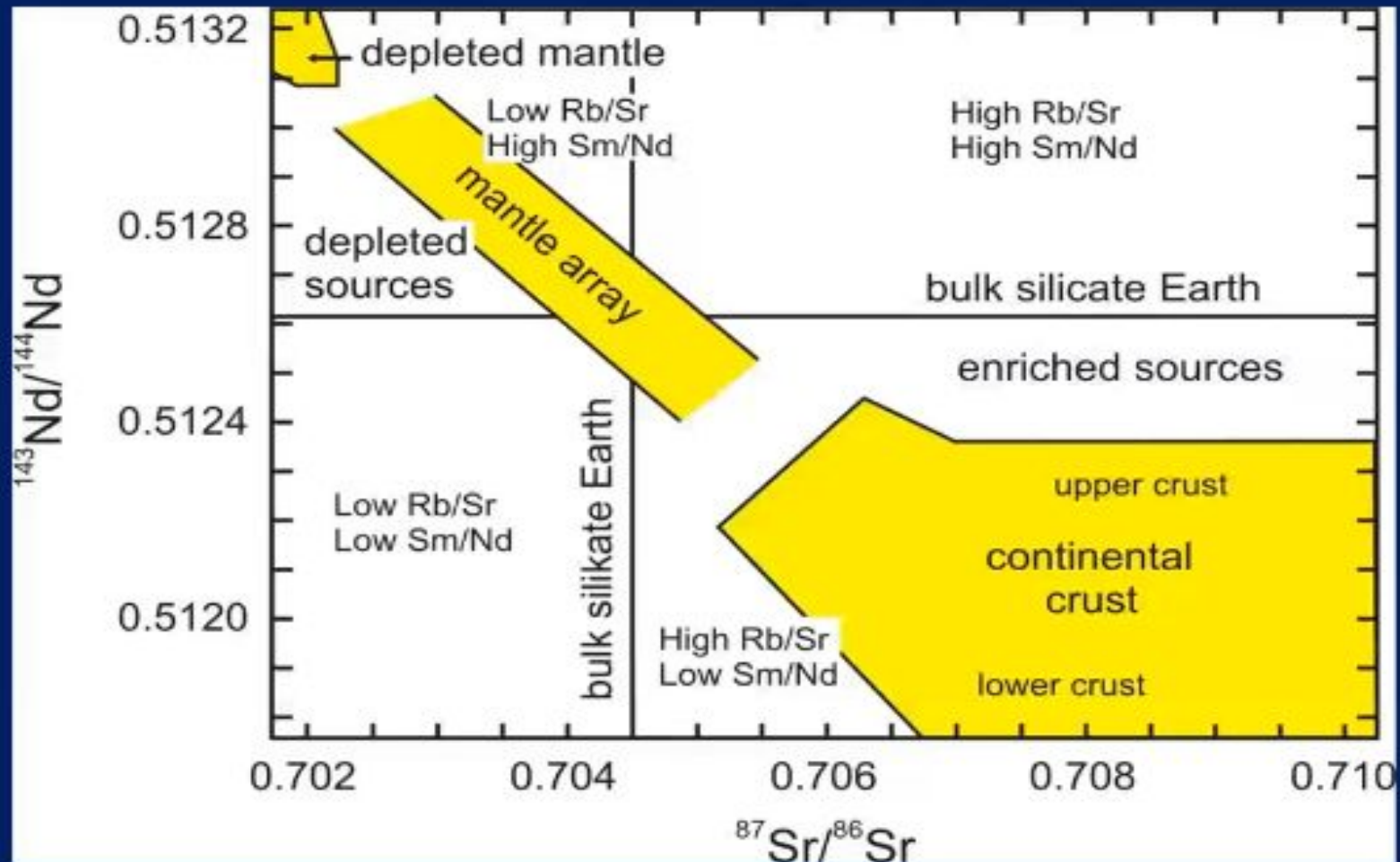


A model age calculated relative to CHUR or DM is the time in the past at which the sample suite separated from the given mantle reservoir and acquired a different Sm/Nd ratio

$$T_{CHUR}^{Nd} = \frac{1}{\lambda} \ln \left(\frac{(^{143}Nd / ^{144}Nd)_{sample, today} - (^{143}Nd / ^{144}Nd)_{CHUR, today}}{(^{147}Sm / ^{144}Nd)_{sample, today} - (^{147}Sm / ^{144}Nd)_{CHUR, today}} + 1 \right)$$

$$T_{DM}^{Nd} = \frac{1}{\lambda} \ln \left(\frac{(^{143}Nd / ^{144}Nd)_{sample, today} - (^{143}Nd / ^{144}Nd)_{DM, today}}{(^{147}Sm / ^{144}Nd)_{sample, today} - (^{147}Sm / ^{144}Nd)_{DM, today}} + 1 \right)$$

Nd-Sr isotope correlation diagram



U, Th and Pb geochemistry

- U and Th are **actinides** (5f orbitals progressively filled)
- Have similar valency (+4) and ionic radii – similar chemical properties – extensively substitute for each other
- **Low abundance in chondritic meteorites** (U = 0.01 ppm, Th = 0.04 ppm)
- Oxidizing condition, U fractionated from Th- forms soluble **Uranyl** (UO_2^{2+}) ion
- During partial melting and fractional crystallization of magma, U and Th concentrated in melt phase and get incorporated into silica-rich products
- Because the continental crust was derived from the partial melting of the upper mantle, it is enriched in U and Th
- **Continental crust - high U and Th**
- **Upper mantle – low U and Th**
- U, Th concentrations in common rock forming minerals low
- Occur primarily in accessory minerals such as **uraninite, thorianite, zircon, thorite, allanite, monazite, apatite, titanite**

The U-Th-Pb isotope system

Isotopes of U-Th-Pb form three important decay systems

			Half life
^{238}U	\longrightarrow	^{206}Pb	4.47 Ga
^{235}U	\longrightarrow	^{207}Pb	704 Ma
^{232}Th	\longrightarrow	^{208}Pb	14.01 Ga

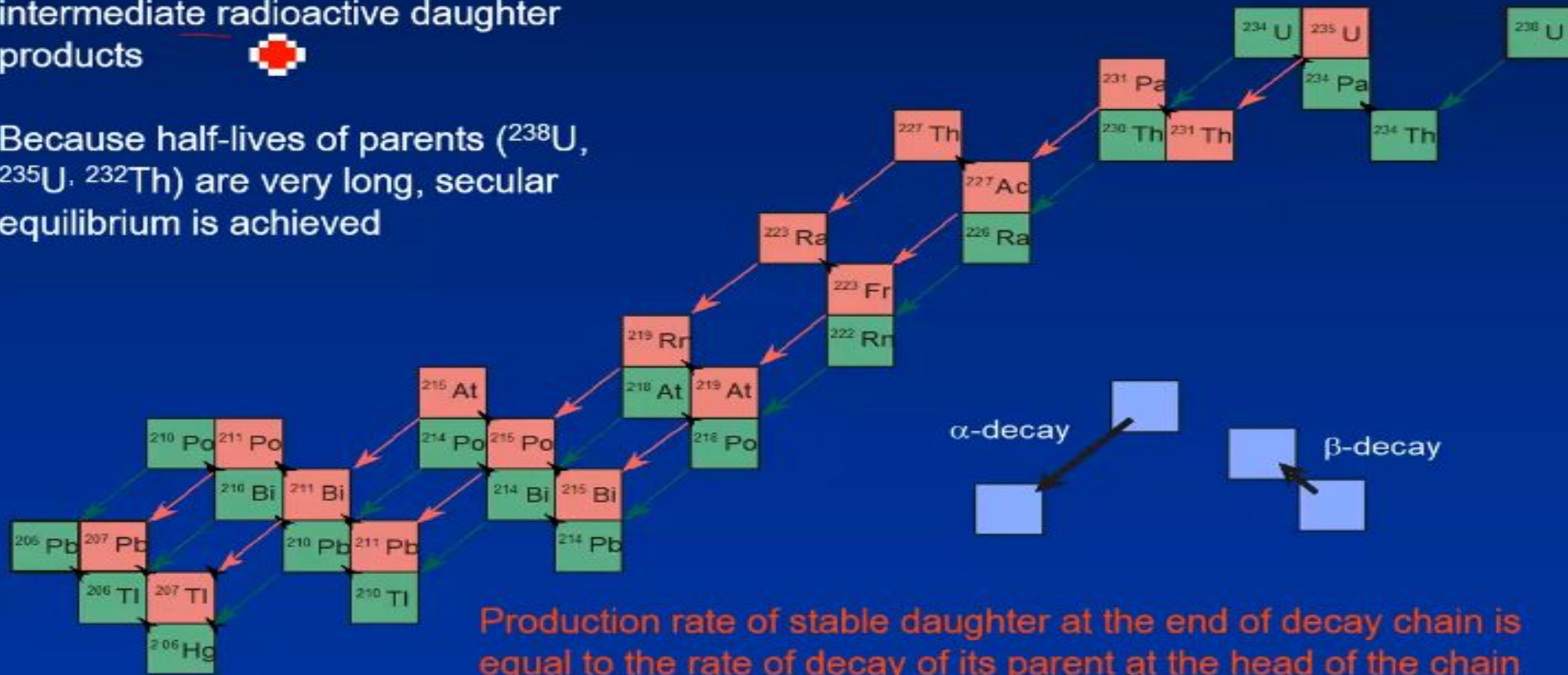
The U-Th-Pb decay series

^{238}U decay-uranium series
 ^{235}U decay-actinium series

The decays take place via many intermediate radioactive daughter products



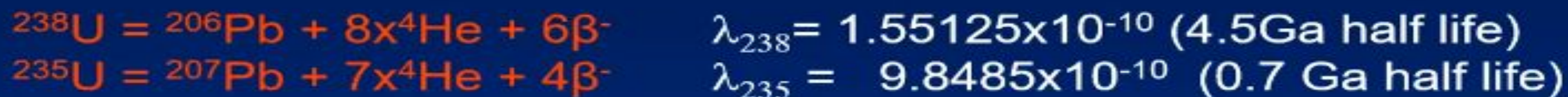
Because half-lives of parents (^{238}U , ^{235}U , ^{232}Th) are very long, secular equilibrium is achieved



Production rate of stable daughter at the end of decay chain is equal to the rate of decay of its parent at the head of the chain

$$\lambda_1 N_1 = \lambda_2 N_2 = \lambda_3 N_3 \dots$$

The U-Pb decay equations



${}^{204}\text{Pb}$ is a stable isotope

${}^{238}\text{U}/{}^{235}\text{U}$ is (nearly) constant in nature = **137.88**

$$\frac{{}^{206}\text{Pb}}{{}^{204}\text{Pb}} = \frac{{}^{206}\text{Pb}_0}{{}^{204}\text{Pb}} + \frac{{}^{238}\text{U}}{{}^{204}\text{Pb}} (e^{\lambda_{238}t} - 1)$$

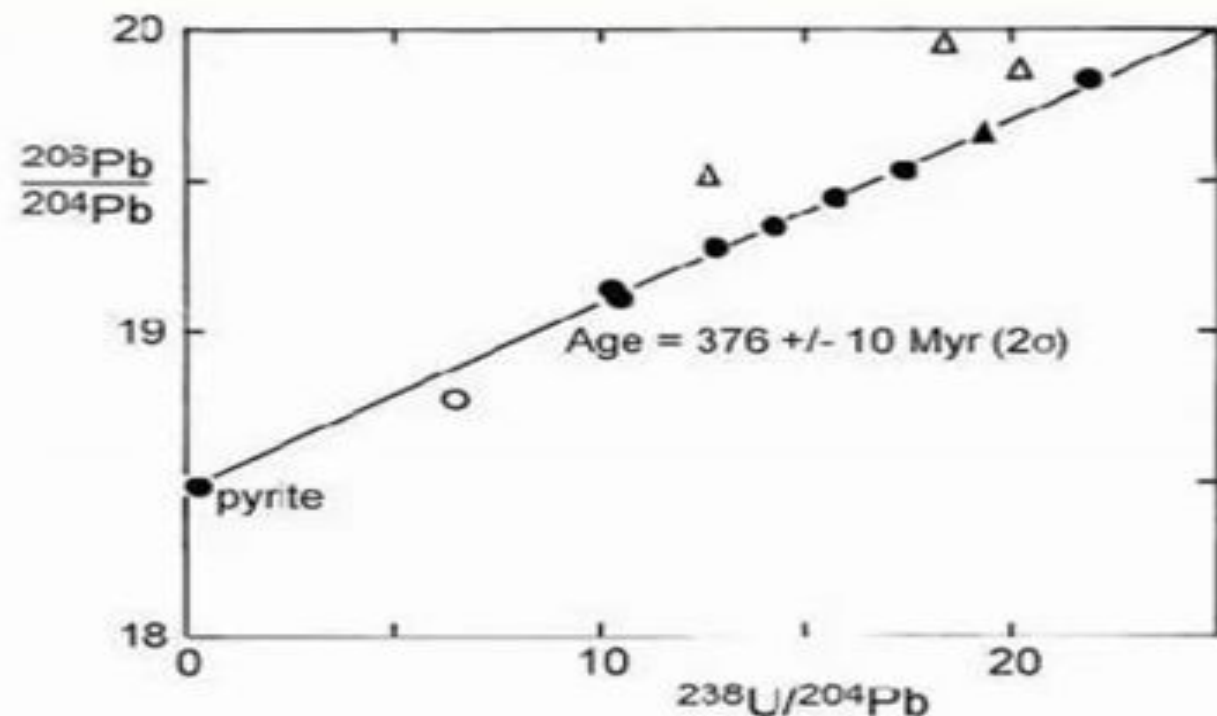
$$\frac{{}^{207}\text{Pb}}{{}^{204}\text{Pb}} = \frac{{}^{207}\text{Pb}_0}{{}^{204}\text{Pb}} + \frac{{}^{235}\text{U}}{{}^{204}\text{Pb}} (e^{\lambda_{235}t} - 1)$$

- These two equations can be used for dating cogenetic and coeval minerals or rocks using the isochron technique
- both systems should give same ages

U-Pb isochrons

- measure many sub-samples with different U/Pb ratios
- results will plot on a straight line if sub-samples of same age

$$\frac{rad}{stable} = \left(\frac{rad}{stable} \right)_i + \left[\frac{parent}{stable} (e^{\lambda t} - 1) \right]$$



Equation in the form:
 $y = mx + b$

Where:

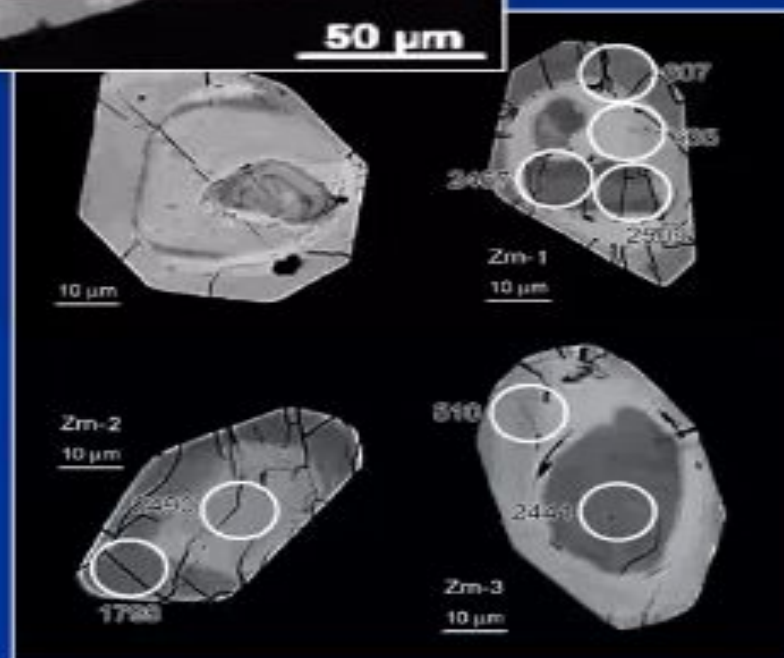
$b = (rad / stable) \text{ at time } 0$

$m = e^{\lambda t} - 1$

Dating of minerals with high U/Pb
e.g., zircon

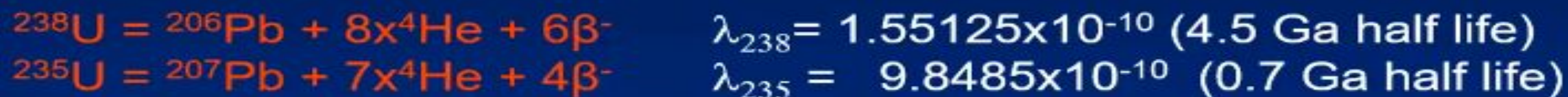
U-Pb dating of zircon

- Zircon is a zirconium silicate (ZrSiO_4) common in granites
- Partitions U, Th into its crystal structure when it grows
- Refractory-survives weathering/ sedimentary recycling, high-grade metamorphism- **retain provenance characteristics**
- In igneous and metamorphic rocks, zircons preserve microtextures, age/ chemical/ isotopic domains related to repeated **phases of growth and reequilibration**
- **ZIRCONS in GRANITE: key to tracking continental crust evolution**



Dating of zircons

- U-Th isotopes in zircon decay to isotopes of Pb



${}^{204}\text{Pb}$ is a stable isotope

${}^{238}\text{U}/{}^{235}\text{U}$ is (nearly) constant in nature = **137.88**

$$\frac{{}^{206}\text{Pb}}{{}^{204}\text{Pb}} = \frac{{}^{206}\text{Pb}_0}{{}^{204}\text{Pb}} + \frac{{}^{238}\text{U}}{{}^{204}\text{Pb}} (e^{\lambda_{238}t} - 1)$$

$$\frac{{}^{207}\text{Pb}}{{}^{204}\text{Pb}} = \frac{{}^{207}\text{Pb}_0}{{}^{204}\text{Pb}} + \frac{{}^{235}\text{U}}{{}^{204}\text{Pb}} (e^{\lambda_{235}t} - 1)$$

Zircon takes in insignificant amount of Pb in its structure when it grows

$${}^{206}\text{Pb}^* = {}^{238}\text{U} (e^{\lambda_{238}t} - 1)$$

$${}^{207}\text{Pb}^* = {}^{235}\text{U} (e^{\lambda_{235}t} - 1)$$

The Wetherill concordia diagram

$$^{206}\text{Pb}^* = ^{238}\text{U} (e^{\lambda_{238}t} - 1)$$

$$^{207}\text{Pb}^* = ^{235}\text{U} (e^{\lambda_{235}t} - 1)$$

$$\frac{^{206}\text{Pb}^*}{^{238}\text{U}} = (e^{\lambda_{238}t} - 1)$$

$$\frac{^{207}\text{Pb}^*}{^{235}\text{U}} = (e^{\lambda_{235}t} - 1)$$

A U-bearing mineral yields concordant dates by solving the above two equations

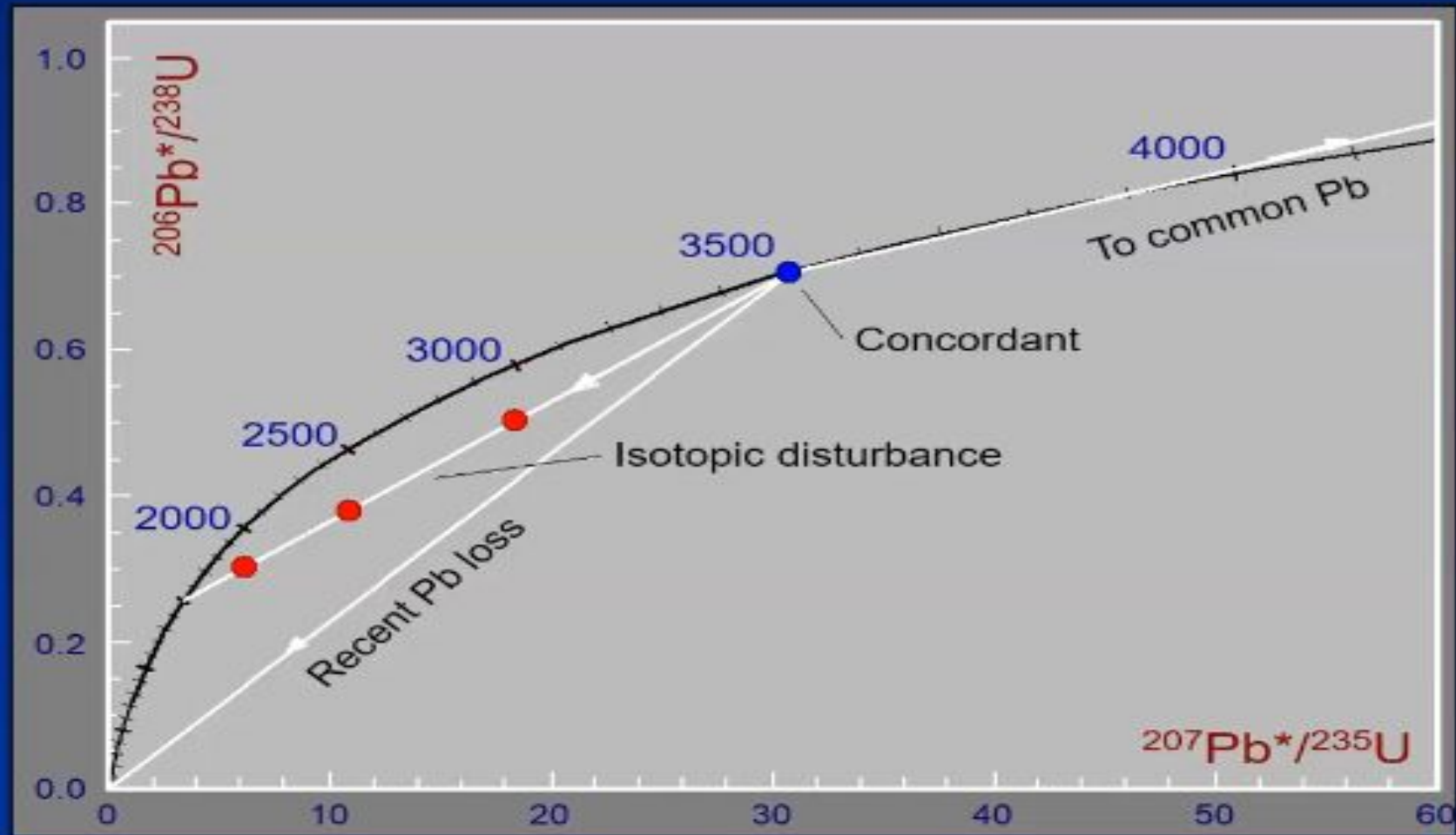
Conversely, can use the two equations to calculate compatible sets of $^{206}\text{Pb}/^{238}\text{U}$ and $^{207}\text{Pb}/^{235}\text{U}$ ratios for specified values of t

These equations are therefore the parametric equations of a curve that is the locus of all concordant U-Pb systems

The Wetherill concordia diagram

The Wetherill concordia

Loss of radiogenic daughter can be detected as discordance



Pb-Pb ages

- In many instances, dates from two systems **not concordant** – open system behavior – loss or gain of U or Pb – effect of Pb loss minimized by calculating an age based on **$^{207}\text{Pb}/^{206}\text{Pb}$ ratio**

$$\frac{\frac{^{207}\text{Pb}}{^{204}\text{Pb}} - \frac{^{207}\text{Pb}_0}{^{204}\text{Pb}_0}}{\frac{^{206}\text{Pb}}{^{204}\text{Pb}} - \frac{^{206}\text{Pb}_0}{^{204}\text{Pb}_0}} = \frac{1}{137.88} \frac{(e^{\lambda_{235}t} - 1)}{(e^{\lambda_{238}t} - 1)}$$

$$\frac{\frac{^{207}\text{Pb}}{^{204}\text{Pb}} - \frac{^{207}\text{Pb}_0}{^{204}\text{Pb}_0}}{\frac{^{206}\text{Pb}}{^{204}\text{Pb}} - \frac{^{206}\text{Pb}_0}{^{204}\text{Pb}_0}} = \frac{\frac{^{207}\text{Pb}^*}{^{204}\text{Pb}}}{\frac{^{206}\text{Pb}^*}{^{204}\text{Pb}}} = \frac{^{207}\text{Pb}^*}{^{206}\text{Pb}^*}$$

$$\frac{^{207}\text{Pb}^*}{^{206}\text{Pb}^*} = \frac{1}{137.88} \frac{(e^{\lambda_{235}t} - 1)}{(e^{\lambda_{238}t} - 1)}$$

Calculate ^{207}Pb - ^{206}Pb ages solely on the basis of Pb isotope composition

The above equation is transcendental - cannot be solved algebraically - can be solved iteratively by a computer

Analytical methods of zircon dating

Requires a mass spectrometer

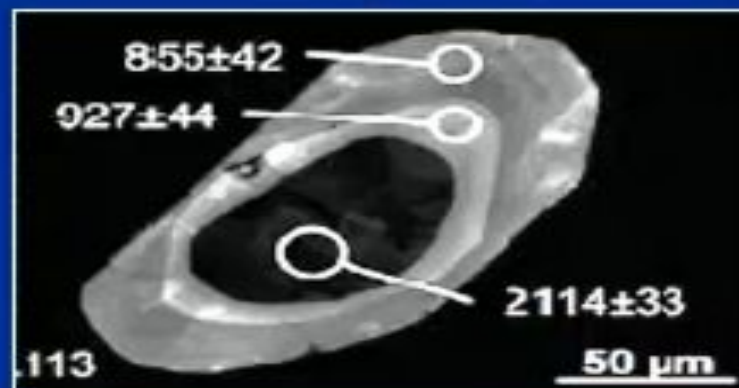
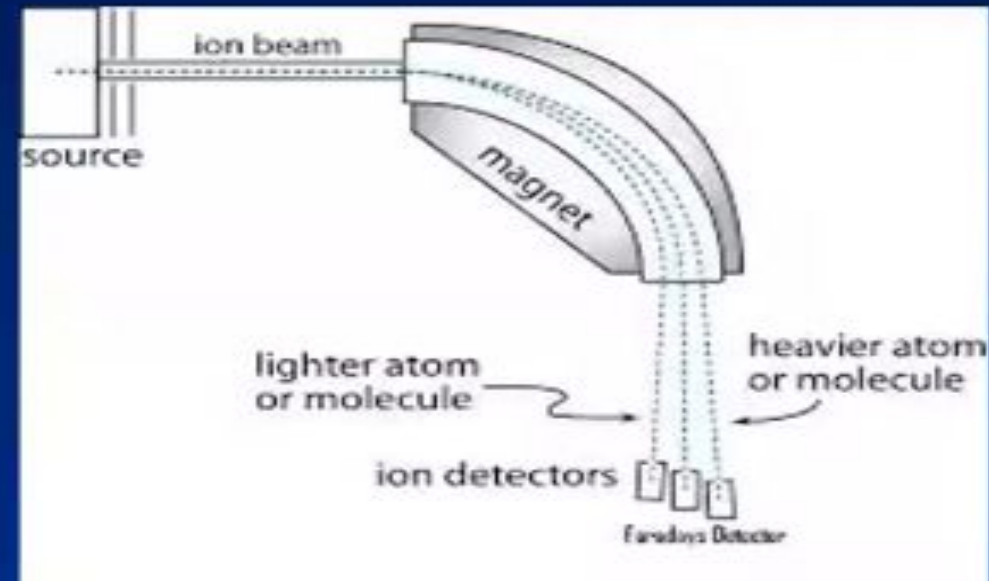
Conventionally, zircon dating was done using **Thermal Ionization Mass Spectrometer (TIMS)**

Involves dissolution of grains in HF, followed by separation of U, Pb and measurement of U-Pb concentrations and isotope ratios using TIMS

Does not work for complex zircons with multiple age components

Laser Ablation Inductively Coupled Plasma Mass Spectrometry (**LA-ICPMS**)

Ion microprobe such as SHRIMP



U-Pb dating of zircon using LA-ICPMS

Radiogenic isotope facility, IIT Kharagpur



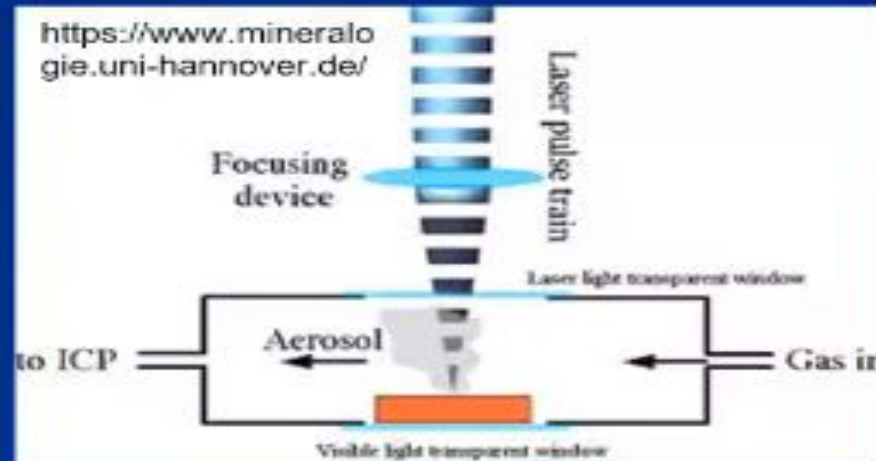
New Wave 193 nm
Excimer Laser
Ablation system

Thermo Fisher
Scientific
quadrupole ICPMS



Trends in Analytical Chemistry, Vol. 24, No. 3, 2005

<https://www.mineralogie.uni-hannover.de/>



uses highly
focused laser light
pulses to remove
(ablate) material
at μm spatial
resolution from
solid sample

Aerosol produced during this process is transferred by a continuous stream of gas into the mass spectrometer for ionization and isotope measurement

U-Pb dating of zircon using LA-ICPMS

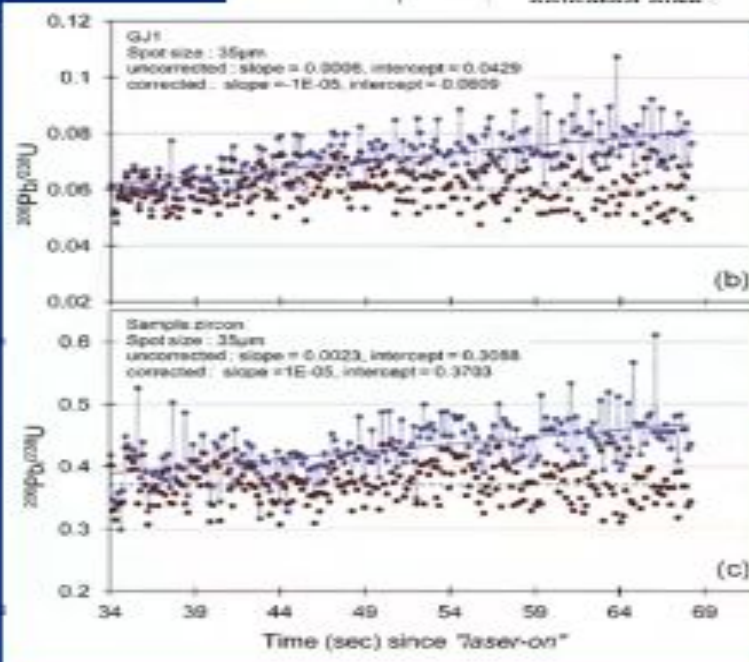
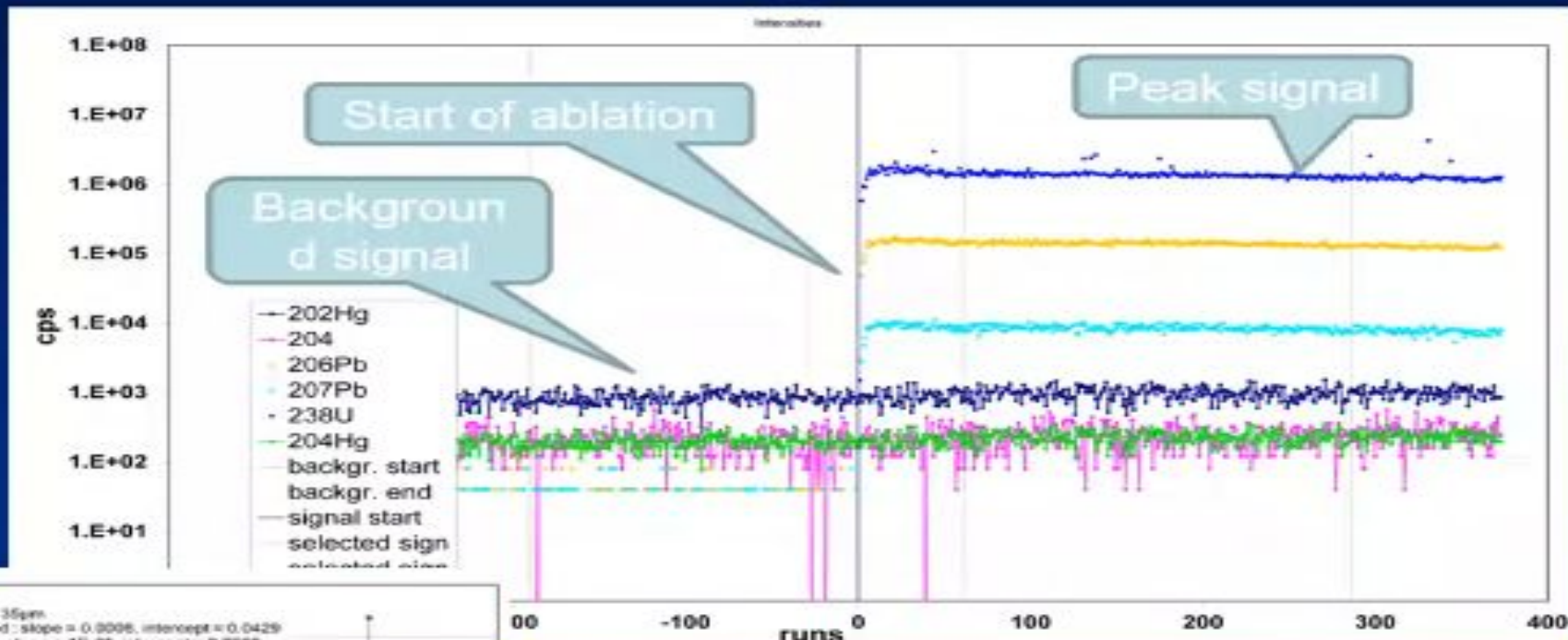
- Data acquired as time-resolved analysis

Masses measured

202-Hg 204-Hg+Pb

206-Pb 207-Pb

238-U



- Correction for laser-induced elemental fractionation (*Sylvester and Ghaderi., 1997, Kosler et al., 2002*)
- Mass-bias and instrument drift correction by external sample bracketing using GJ-1 reference zircon (*Jackson et al., 2004*)

The following Rb-Sr isotope data were measured on a lamprophyre intrusive into the Prakasam alkaline province in southern India at 1321 Ma: Rb=53 ppm, Sr=613 ppm, $^{87}\text{Sr}/^{86}\text{Sr}=0.708637$. Calculate the initial $^{87}\text{Sr}/^{86}\text{Sr}$ of the lamprophyre. Use the following data wherever required.

Isotope	^{84}Sr	^{86}Sr	^{87}Sr	^{88}Sr
Exact mass	83.9134	85.9093	86.9089	87.9056
Ratio to ^{86}Sr	0.05658	1	2.72881	8.3752

$^{85}\text{Rb}/^{87}\text{Rb}=2.5927$, Average atomic weight of Rb=85.4678, $\lambda^{87}\text{Rb}=1.42 \times 10^{-11} \text{ year}^{-1}$