

Zircon Penn Maryland Materials Quarry

**U-Th-Pb radioaktivni sustav**

# U-Th-Pb sistematika

U, Th i Pb su visoko inkompatibilni elementi pa se koncentriraju u materijalima Kore, a osiromašeni (depleted) su u Plaštu.

(U i Th imaju izrazito visoku valenciju a Pb iznimno veliki ionski radijus)

Ionski radijusi i valencije U, Th i Pb u mineralima

Torij stabilan u valenciji  $\text{Th}^{4+}$ , olovo kao  $\text{Pb}^{2+}$ .

Element	Charge	Radius (Å)
U	+4 (+6) oxic	1.05
Th	+4	1.10
Pb	+2	1.32

Material	U(ppm)	Th	Pb
Chondrites	0.01	0.04	1.0
Troilite	.009	<.01	5.9
Basalt	0.43	1.6	3.7
Galena	trace	trace	HUGE
Zircon	HUGE	HUGE	trace
Carbonates	1.9	1.2	5.6
Seawater (surface)	3 ppb	20 fg/g	2.7 pg/g
Seawater (deep)	3 ppb	60 fg/g	5 pg/g



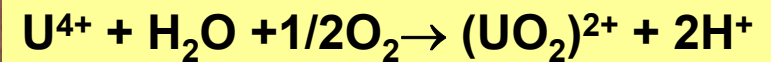
Galinit,  $\text{PbS}$

# Geokemija urana

**Karnotit,**  
 **$K_2(UO_2)_2V_2O_8 \cdot 3(H_2O)$**



Colorado plateau,  
Uranska ležišta



Djelovanjem kisika i vode reduktivni oblik urana (4+) oksidacijom prelazi u 6+ a hidrolizom u uranil  $(UO_2)^{2+}$  ion.

# U, Th u mineralima i stijenama



Apatit,  $\text{Ca}_5(\text{PO}_4)_3(\text{OH}, \text{F}, \text{Cl})$



Monacit,  $(\text{Ce}, \text{La}, \text{Nd}, \text{Th})\text{PO}_4$



Torit,  $\text{ThSiO}_4$



Torijanit,  $\text{ThO}_2$



Ksenotim,  $\text{YPO}_4$



Titanit,  $\text{CaTiSiO}_5$

# Sadržaj urana, torija i olova u magmatskim i sedimentnim stijenama

Table 12.1 Average Concentrations of U, Th, and Pb in Igneous and Sedimentary Rocks (Turekian and Wedepohl, 1961)

ROCK TYPE	U ppm	Th ppm	Pb ppm	$\frac{\text{Th}}{\text{U}}$	$\frac{\text{U}}{\text{Pb}}$
Low-Ca granite	3.0	17.	19.	5.7	0.16
High-Ca granite	3.0	8.5	15.	2.8	0.20
Syenite	3.0	13.	12.	4.3	0.25
Basaltic rocks	1.0	4.0	6.	4.0	0.17
Ultramafics	0.001	0.004	1.0	4.0	0.001
Shale	3.7	12.	20.	3.3	0.18
Sandstone	0.45	1.7	7.	3.8	1.73
Carbonates	2.2	1.7	9.	0.77	0.24
Deep sea clay	1.3	7.	80.	5.4	0.016



Betafit,  $(\text{Ca,U})_2(\text{Ti,Nb,Ta})_2\text{O}_6(\text{OH})$



Rössing, najveće U-ležište na Svijetu u granitoidima, Namibija

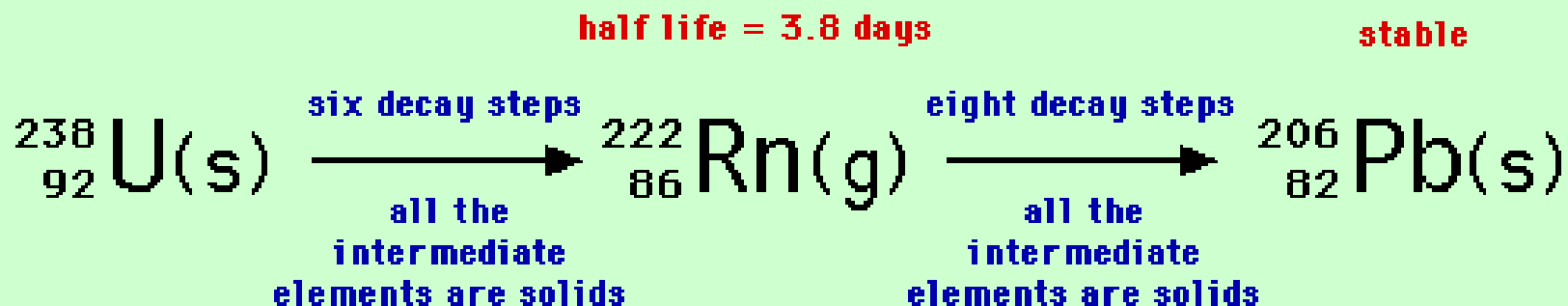
# Radioaktivni raspad urana i torija

Table 12.2 Abundances, Half-Lives, and Decay Constants of the Principal Naturally Occurring Isotopes of Uranium and Thorium

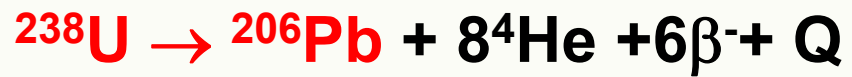
ISOTOPE	ABUNDANCE %	HALF-LIFE y	DECAY CONSTANT $y^{-1}$	REFERENCE
$^{238}\text{U}$	99.2739	$4.510 \times 10^9$	$1.537 \times 10^{-10}$	1
		$4.468 \times 10^9$	$1.55125 \times 10^{-10}$	2
$^{235}\text{U}$	0.7204	$0.7129 \times 10^9$	$9.722 \times 10^{-10}$	3
		$0.7038 \times 10^9$	$9.8485 \times 10^{-10}$	2
$^{234}\text{U}$	0.0057	$2.48 \times 10^5$	$2.806 \times 10^{-6}$	4
$^{232}\text{Th}$	100	$13.890 \times 10^9$	$4.990 \times 10^{-11}$	5
		$14.008 \times 10^9$	$4.948 \times 10^{-11}$	6

1. Kovarik and Adams (1955)
2. Jaffey et al. (1971)
3. Fleming et al. (1952)
4. Strominger et al. (1958)
5. Picciotto and Wilgain (1956)
6. LeRoux and Glendenin (1963)

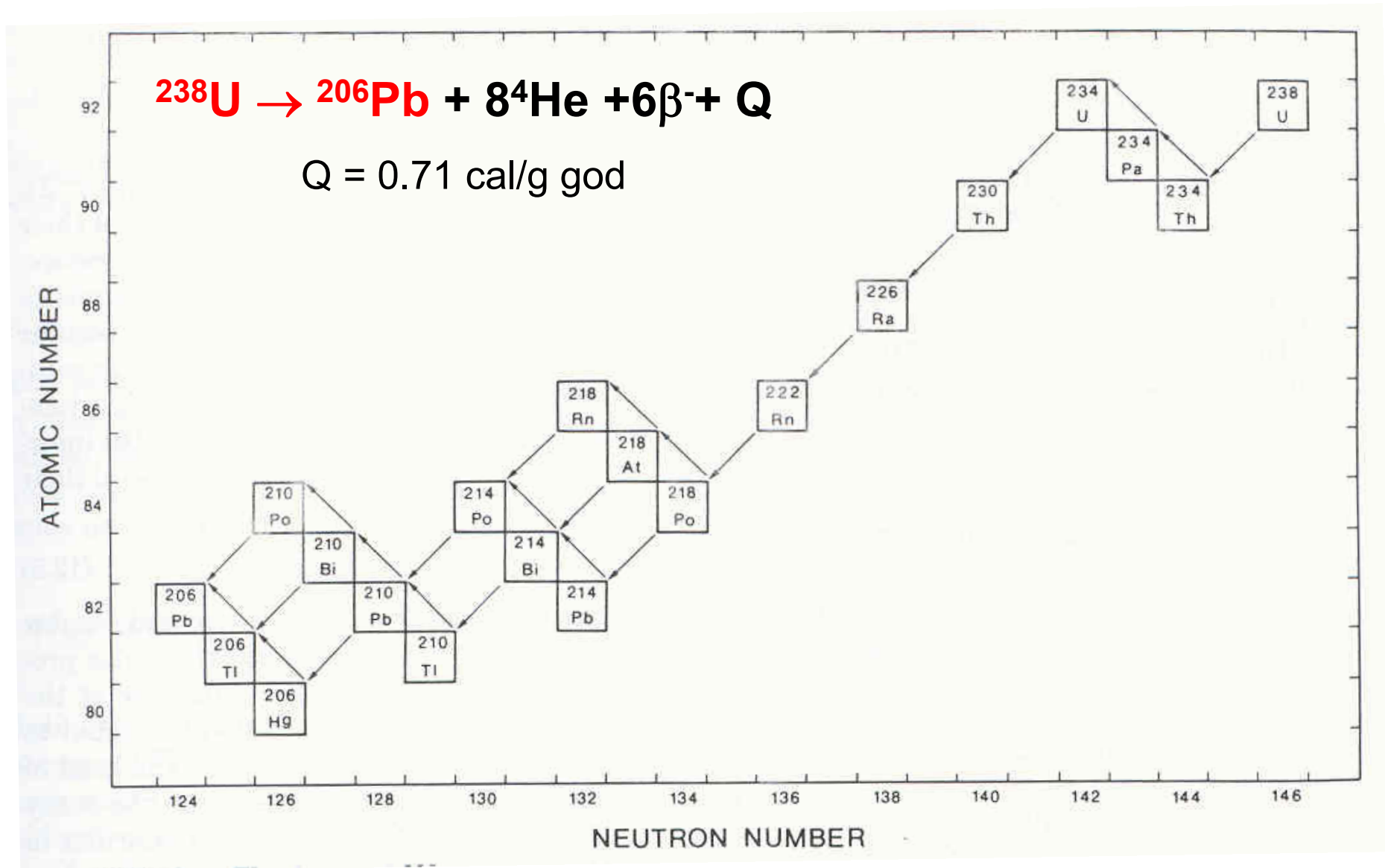
Rasprostranjenje, polu-  
život, konstanta radio-  
aktivnog raspada glavnih,  
prirodno zastupljenih izo-  
topa urana i torija



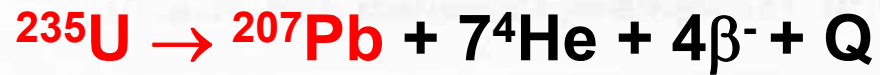
# Tablica radioaktivnog raspadanja $^{238}\text{U}$



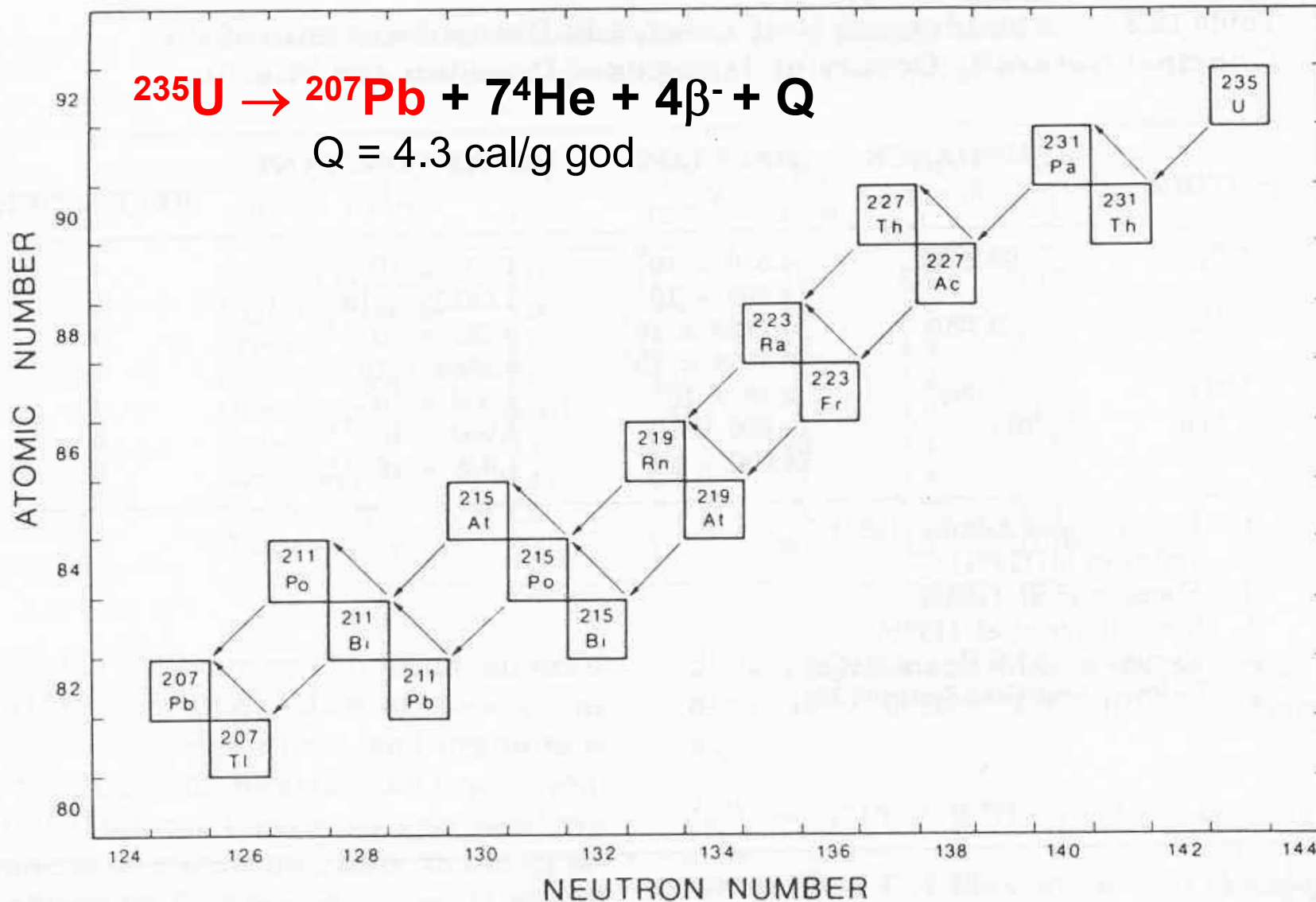
$$Q = 0.71 \text{ cal/g god}$$



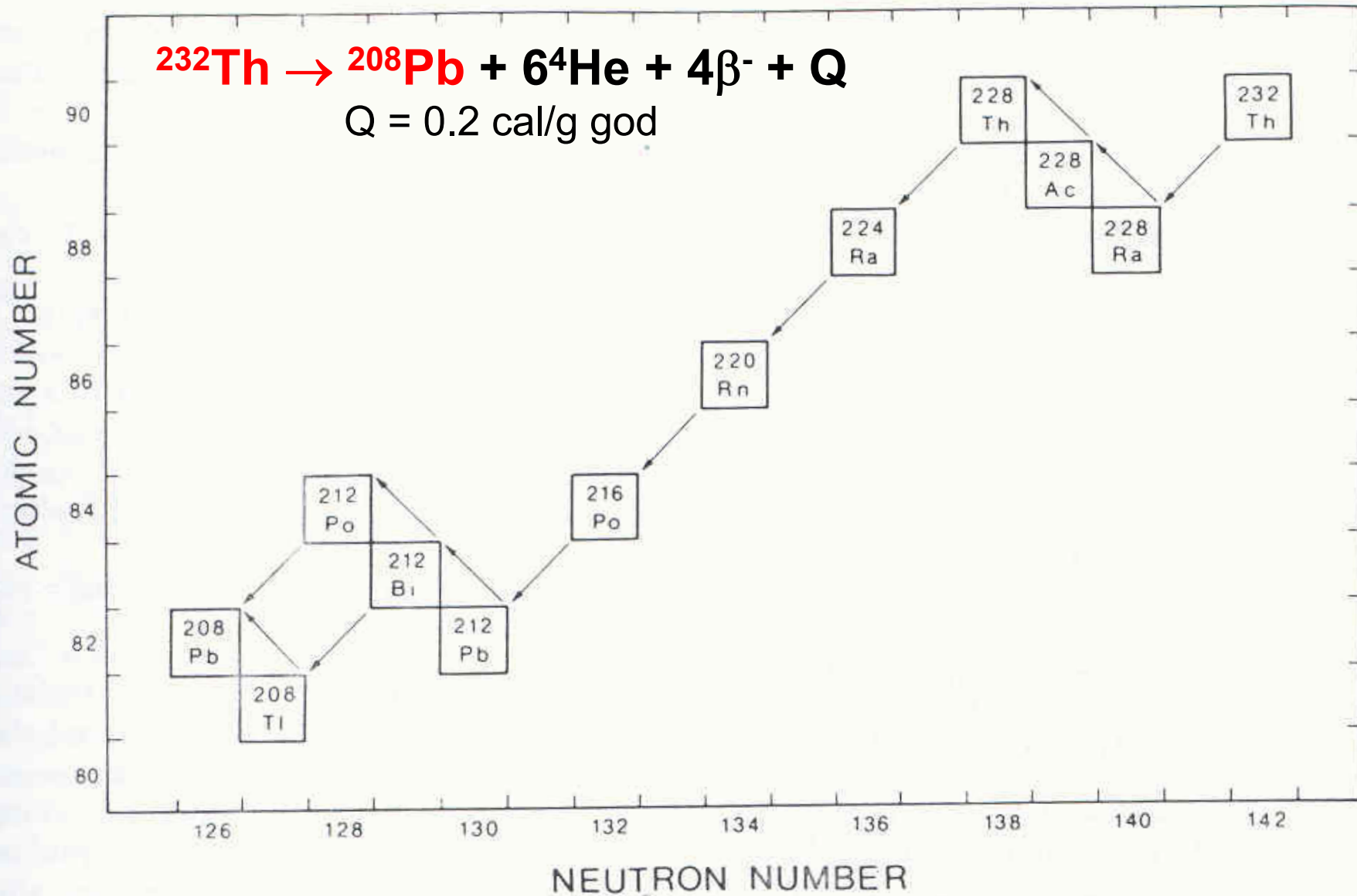
# Tablica radioaktivnog raspada $^{235}\text{U}$



$Q = 4.3 \text{ cal/g god}$



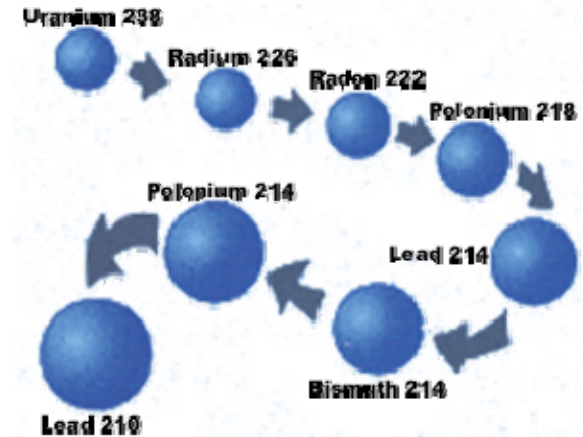
# Tablica radioaktivnog raspada $^{232}\text{Th}$



# Sekularna ravnoteža

Uvjet za točno određivanje starosti je *sekularna ravnoteža* i neporemećeni radioaktivni niz s nekim geološkim ili geokemijskim događajem

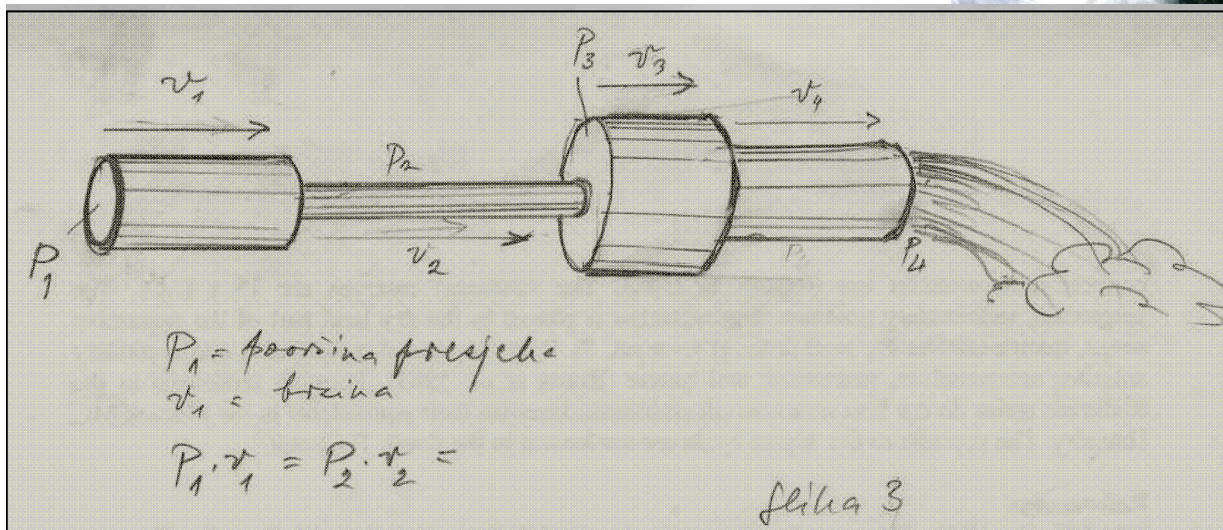
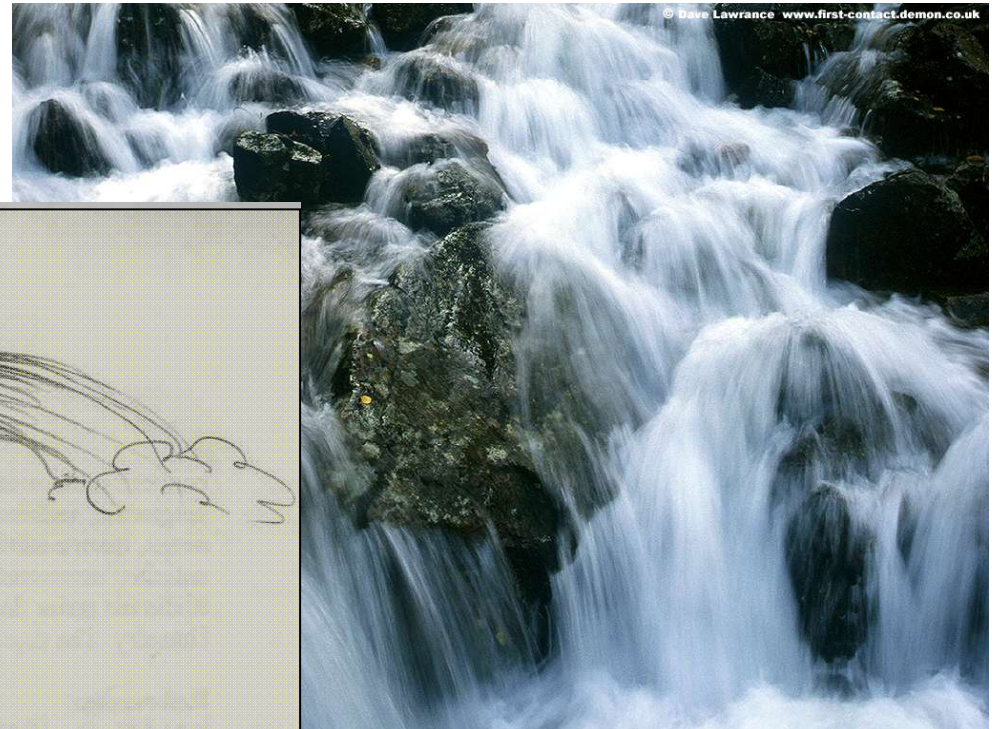
$$N_1\lambda_1 = N_2\lambda_2 = N_3\lambda_3 = \dots = N_{18}\lambda_{18}$$



Usporedivo sa protokom vode kroz cijevi različitih promjera

$$P_1v_1 = P_2v_2 = P_3v_3 = P_4v_4$$

P = površina presjeka  
v = brzina vode



# Sekularna ravnoteža

Ako je  $T_{1/2}$  roditelja  $\gg \gg T_{1/2}$  djece:

na primjer:  $^{238}\text{U}$ ,  $T_{1/2} = 4.510 \times 10^9$  god. , a najduži  $T_{1/2}$  radioaktivnog djeteta  $^{234}\text{U} = 2.48 \times 10^5$  god.

Onda možemo aproksimirati:



Olovo ima četiri izotopa:

Tri stabilna  $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$ ,  $^{208}\text{Pb}$  i

radioaktivni  $^{210}\text{Pb} \rightarrow ^{210}\text{Bi} \rightarrow ^{210}\text{Po} \rightarrow ^{206}\text{Pb}$  ( $T_{1/2} = 138$  god. !!! pa ga tretiramo kao stabilnog)

# U-Th-Pb vremenske jednačbe

Modelne starosti:

$$\frac{{}^{206}\text{Pb}}{{}^{204}\text{Pb}} = \left( \frac{{}^{206}\text{Pb}}{{}^{204}\text{Pb}} \right)_i + \frac{{}^{238}\text{U}}{{}^{204}\text{Pb}} (e^{\lambda t} - 1)$$

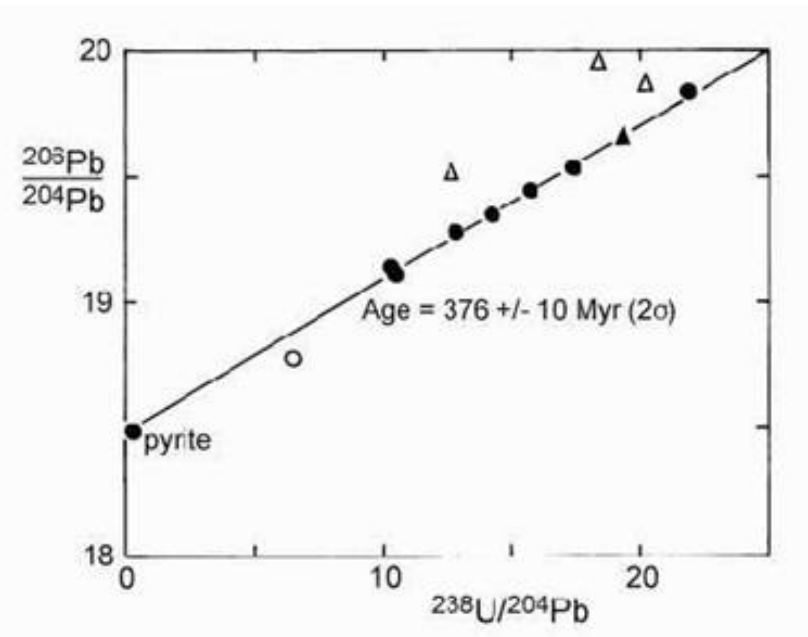
$$\frac{{}^{207}\text{Pb}}{{}^{204}\text{Pb}} = \left( \frac{{}^{207}\text{Pb}}{{}^{204}\text{Pb}} \right)_i + \frac{{}^{235}\text{U}}{{}^{204}\text{Pb}} (e^{\lambda t} - 1)$$

$$\frac{{}^{208}\text{Pb}}{{}^{204}\text{Pb}} = \left( \frac{{}^{208}\text{Pb}}{{}^{204}\text{Pb}} \right)_i + \frac{{}^{232}\text{Th}}{{}^{204}\text{Pb}} (e^{\lambda t} - 1)$$

\* Olovo  ${}^{204}\text{Pb}$  korišteno kao referentni izotop

Starosti iz sva tri sistema se mogu podudarati, zovemo ih KONKORDANTE starosti.

Uvjerljivije starosti se postižu metodom «izokrone»



After Smith and Farquhar (1989)

If  $x = ({}^{238}\text{U}/{}^{204}\text{Pb})_m$

And  $y = ({}^{206}\text{Pb}/{}^{204}\text{Pb})_m$

We have  $y = b + mx$

Where intercept  $b = ({}^{206}\text{Pb}/{}^{204}\text{Pb})_i$

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

# U-Th-Pb vremenske jednačbe

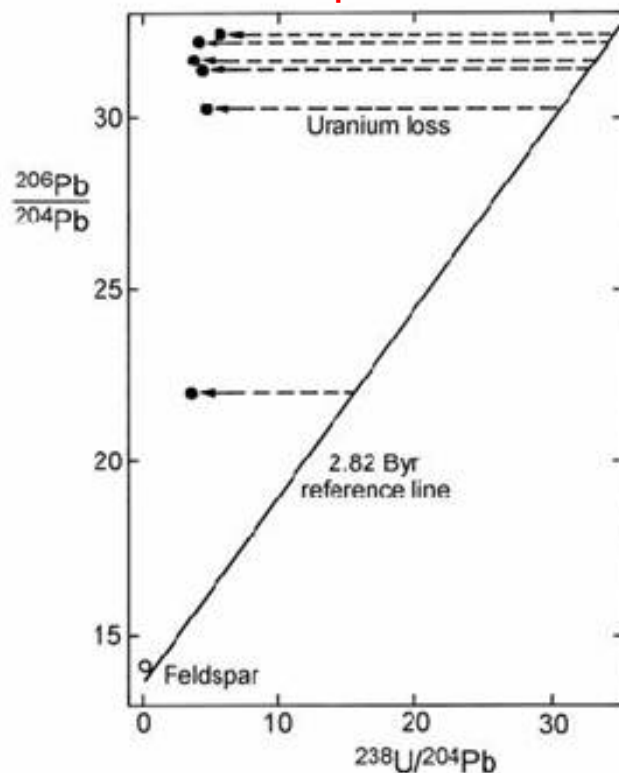
## Ponašanje otvorenog sustava

### Problem:

Koji procesi mogu U-Th-Pb sustav učiniti DISKORDANTNIM?

### Rješenje

#### Simptomi



Th-Pb starost = 2.82 Ga ali  $^{238}\text{U}$ - $^{206}\text{Pb}$  starost izmijenjena je zbog gubitka urana.

Koristeći činjenicu da postoje dva radioaktivna izotopa U, sa svojom vlastitom djecom, .....i da je  $^{238}\text{U}/^{235}\text{U} = 137.88$  u današnje vrijeme, kombiniramo  $^{235}\text{U}$  i  $^{238}\text{U}$  radioaktivne jednačbe u:

$$\frac{\left(\frac{^{207}\text{Pb}}{^{204}\text{Pb}}\right) - \left(\frac{^{207}\text{Pb}}{^{204}\text{Pb}}\right)_i}{\left(\frac{^{206}\text{Pb}}{^{204}\text{Pb}}\right) - \left(\frac{^{206}\text{Pb}}{^{204}\text{Pb}}\right)_i} = \frac{1}{137.88} \left( \frac{e^{\lambda_5 t} - 1}{e^{\lambda_8 t} - 1} \right)$$

\* ova jednačba vrijedi za gubitak Pb ili U u današnje vrijeme.

#### Opaska:

Jednačba spada u transcendentne jednačbe i ne može se riješiti za  $t$ , rješenje je moguće grafički ili iterativnim putem uz prvu pretpostavljenu vrijednost smanjujući postupno razliku prema pravoj vrijednosti.

# Evolucija radiogenog $(^{207}\text{Pb}/^{206}\text{Pb})^*$ za različite vrijednosti t

$$\left(\frac{^{207}\text{Pb}}{^{206}\text{Pb}}\right)^* = \frac{1}{137.88} \left(\frac{e^{\lambda_5 t} - 1}{e^{\lambda_8 t} - 1}\right)$$

Rješenje transcendentale jednadžbe

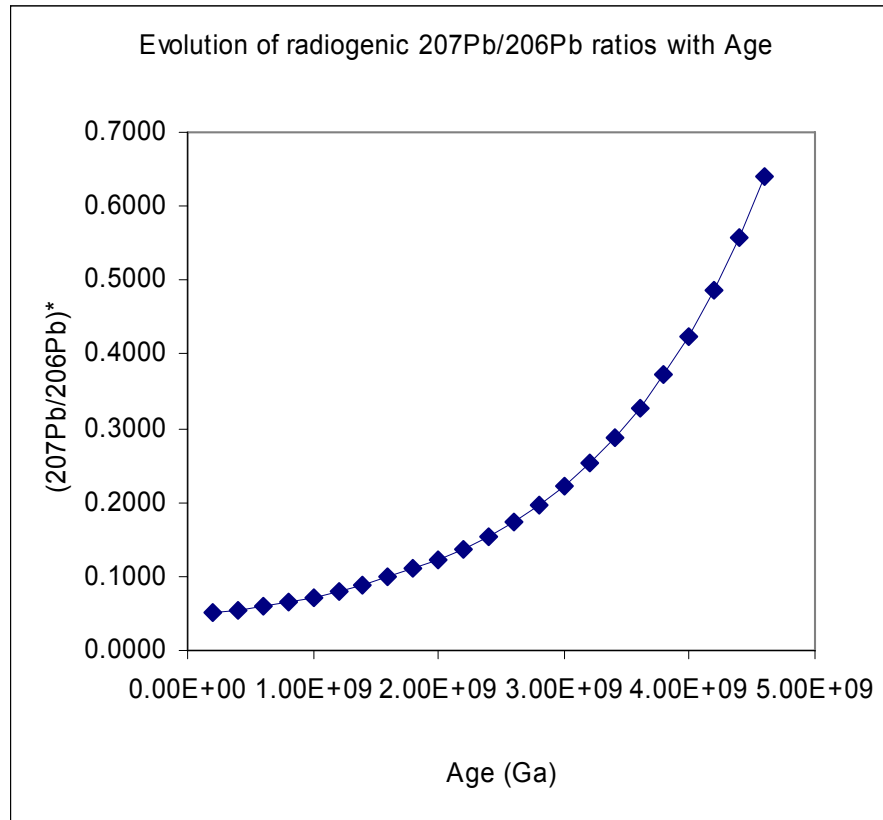


Table of  $(^{207}\text{Pb}/^{206}\text{Pb})^*$  values for different t

Age (yr)	num	den	$^{207}\text{Pb}/^{206}\text{Pb}$
0	--	--	--
2.00E+08	0.22	0.03	0.0501
4.00E+08	0.48	0.06	0.0547
6.00E+08	0.81	0.10	0.0599
8.00E+08	1.20	0.13	0.0658
1.00E+09	1.68	0.17	0.0725
1.20E+09	2.26	0.20	0.0801
1.40E+09	2.97	0.24	0.0888
1.60E+09	3.83	0.28	0.0987
1.80E+09	4.89	0.32	0.1101
2.00E+09	6.17	0.36	0.1230
2.20E+09	7.73	0.41	0.1379
2.40E+09	9.63	0.45	0.1549
2.60E+09	11.95	0.50	0.1744
2.80E+09	14.76	0.54	0.1969
3.00E+09	18.20	0.59	0.2227
3.20E+09	22.38	0.64	0.2525
3.40E+09	27.46	0.69	0.2868
3.60E+09	33.66	0.75	0.3265
3.80E+09	41.21	0.80	0.3723
4.00E+09	50.40	0.86	0.4252
4.20E+09	61.59	0.92	0.4864
4.40E+09	75.22	0.98	0.5574
4.60E+09	91.81	1.04	0.6396

What is the ratio of  $(^{207}\text{Pb}/^{206}\text{Pb})^*$  at t=0?

# Pb-Pb izokrone

## *Geokrona ili starost meteorita i Zemlje*



Canyon Diablo meteorit

Patterson (1956) testirao pretpostavku da su:

1. Meteoriti i Zemlja nastali u isto vrijeme
2. Pb izotopi u meteoritu predstavnici «cijelo-zemljinog» (bulk-earth) Pb odnosa.



# Pb-Pb izokrone

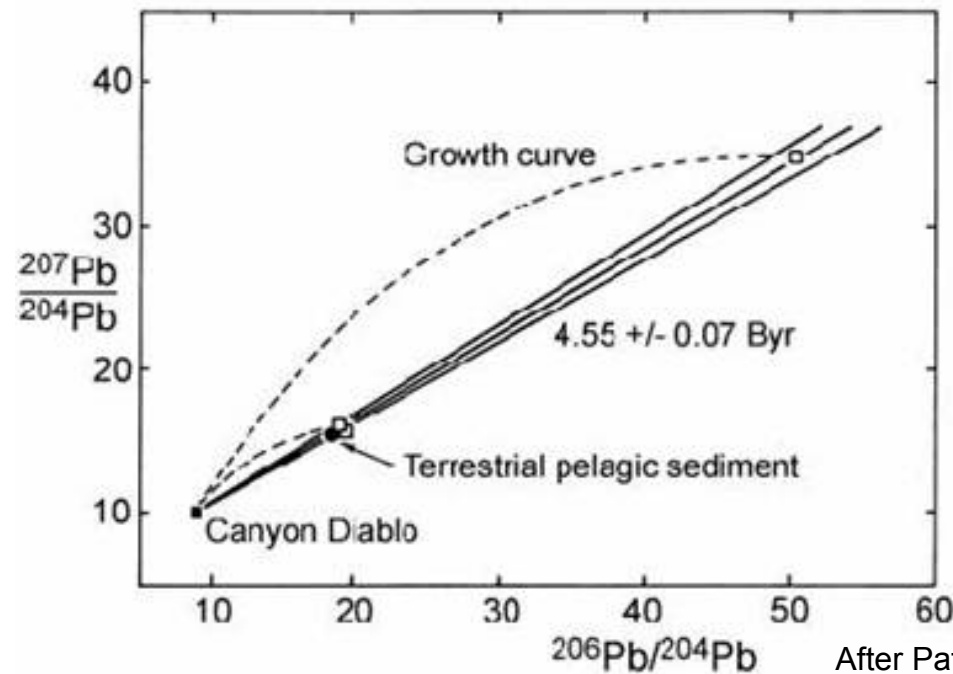
## Geokrona ili starost meteorita i Zemlje

$$\frac{\left(\frac{^{207}\text{Pb}}{^{204}\text{Pb}}\right) - \left(\frac{^{207}\text{Pb}}{^{204}\text{Pb}}\right)_i}{\left(\frac{^{206}\text{Pb}}{^{204}\text{Pb}}\right) - \left(\frac{^{206}\text{Pb}}{^{204}\text{Pb}}\right)_i} = \frac{1}{137.88} \left( \frac{e^{\lambda_5 t} - 1}{e^{\lambda_8 t} - 1} \right)$$

If  $x = (^{206}\text{Pb}/^{204}\text{Pb})_m$   
 And  $y = (^{207}\text{Pb}/^{204}\text{Pb})_m$   
 We have  $y = mx + (y_0 + x_0)$

Where  $(y_0, x_0)$  = primordial Pb isotopic composition

And slope  $m = \frac{1}{137.88} \left( \frac{e^{\lambda_5 t} - 1}{e^{\lambda_8 t} - 1} \right)$

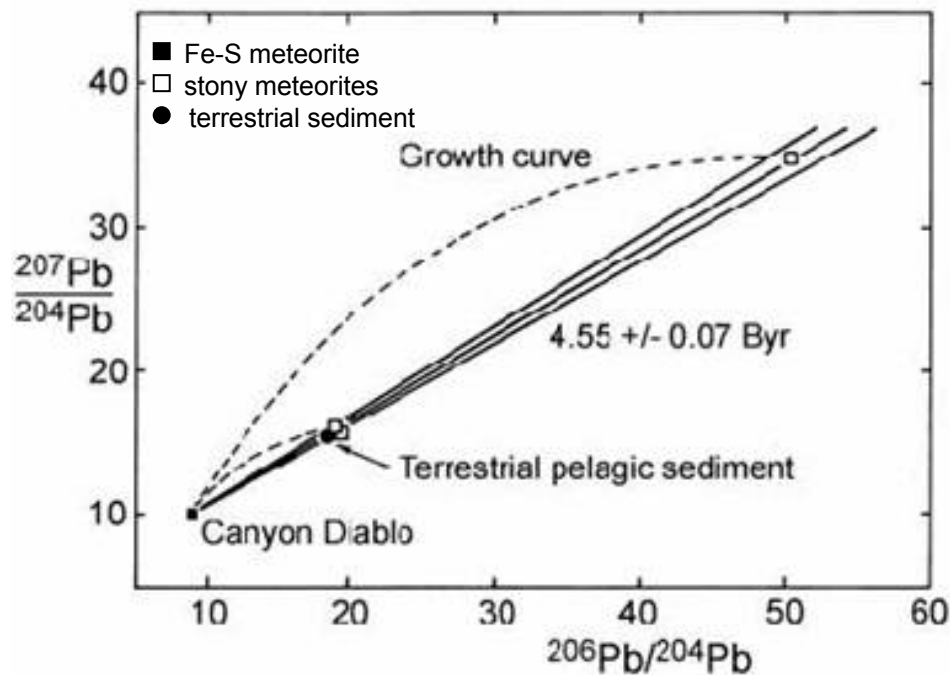


# Pb-Pb izokrone

## Geokrona ili starost meteorita i Zemlje

$$\frac{(^{207}\text{Pb}/^{204}\text{Pb} - b_0)}{(^{207}\text{Pb}/^{204}\text{Pb} - a_0)} = 1/137.8 \left[ \frac{e^{\lambda T} - 1}{e^{\lambda T} - 1} \right]$$

$a_0, b_0 = ^{207}\text{Pb}/^{204}\text{Pb}$ ,  $^{207}\text{Pb}/^{204}\text{Pb}$  Praischkonsko olovo  
 $T = \text{starost Zemlje, } 4.55 \pm 0.07 \times 10^9 \text{ god.}$   
 $\lambda_1 = 1.537 \times 10^{-10}$ ,  $\lambda_2 = 9.72 \times 10^{-10} \text{ god.}$



### Isotopni odnosi u Canyon Diablo meteoritu:

$^{206}\text{Pb}/^{204}\text{Pb}$	9.3066
$^{207}\text{Pb}/^{204}\text{Pb}$	10.293
$^{208}\text{Pb}/^{204}\text{Pb}$	29.475



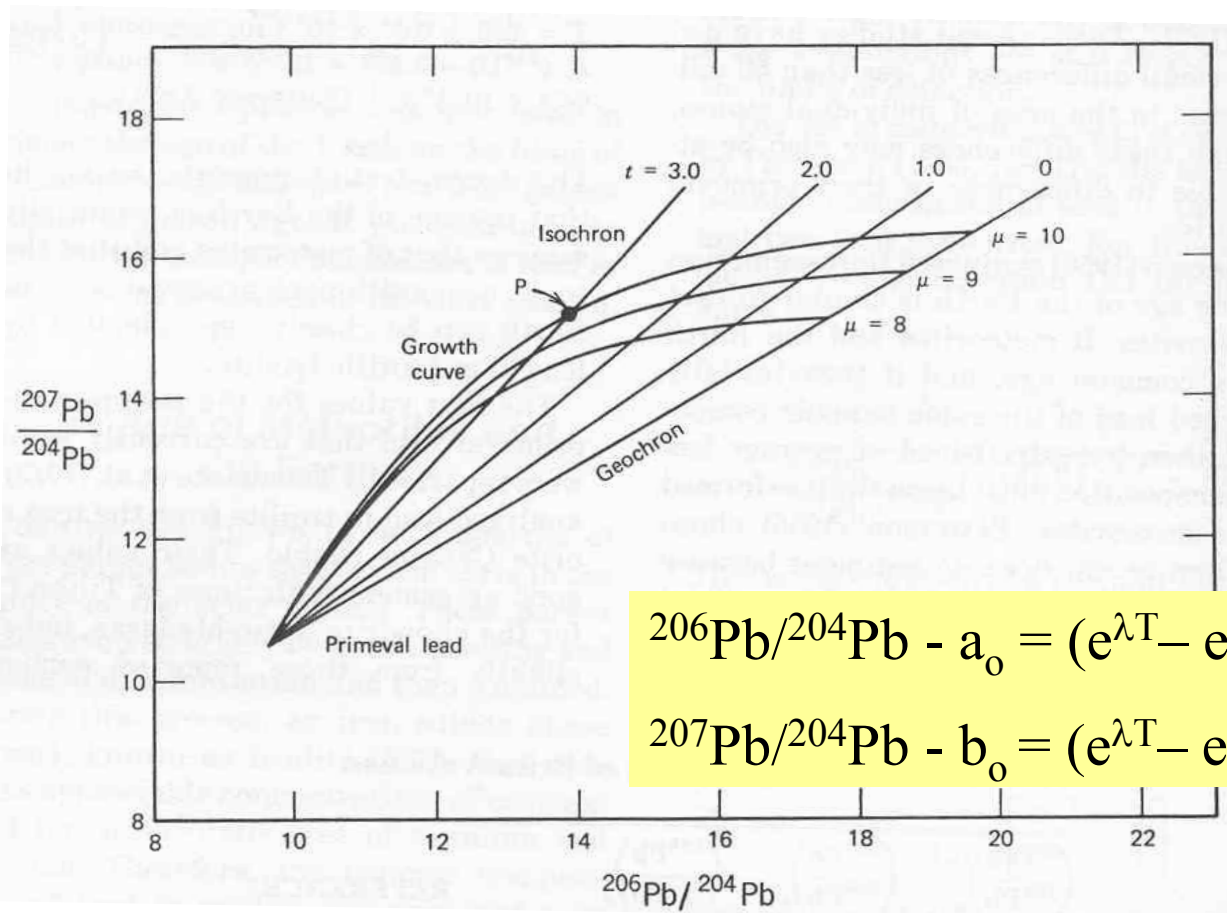
# Metoda «zajedničkog» olova

## Common lead model

**Holmes-Houtermanov model** *jednostupnog* razvoja Pb izotopa na Zemlji

Datiranje «zajedničkog» olova:

Grafička prezentacija Holmes-Houtermanova modela



$$m = \frac{1}{137,8} \left[ \frac{e^{\lambda 2T} - e^{\lambda 2t}}{e^{\lambda 1T} - e^{\lambda 1t}} \right]$$

za t=0

$$m = \frac{1}{137,8} \left[ \frac{e^{\lambda 2T} - 1}{e^{\lambda 1T} - 1} \right]$$

geokrona

$$^{206}\text{Pb}/^{204}\text{Pb} - a_0 = (e^{\lambda T} - e^{\lambda t})$$

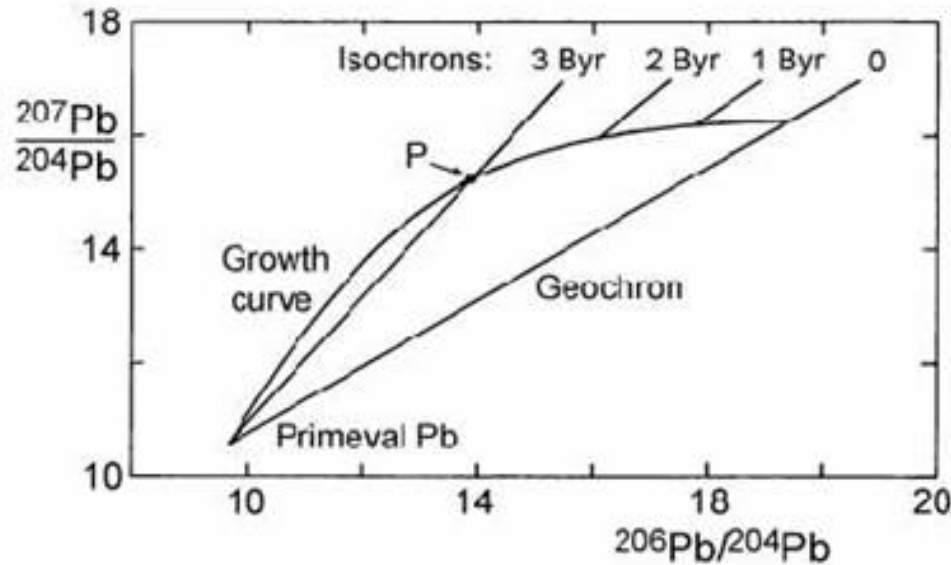
$$^{238}\text{U}/^{204}\text{Pb} = \mu$$

$$^{207}\text{Pb}/^{204}\text{Pb} - b_0 = (e^{\lambda T} - e^{\lambda t})$$

$$^{235}\text{U}/^{204}\text{Pb} = \mu/137.8$$

# Metoda «zajedničkog» olova

## Common lead model



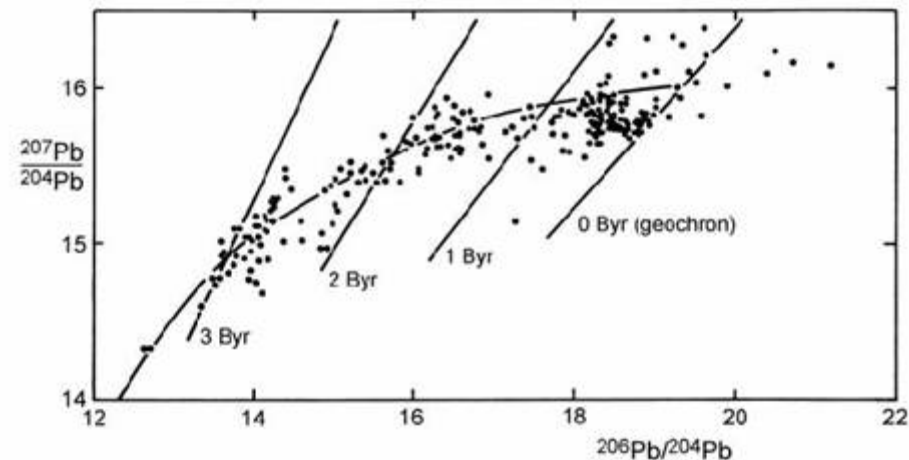
### Interpretations:

- 1) All galenas that formed at 3Ga, regardless of the  $\mu$  of their sources, will plot on an isochron.
- 2) For  $t=0$  (present), Geochron: all single-stage galenas and meteorites plot on it.
- 3) Note that given an age and isotope ratios, one can calculate  $\mu$  from:

$$\left(\frac{^{206}\text{Pb}}{^{204}\text{Pb}}\right)_t = \left(\frac{^{206}\text{Pb}}{^{204}\text{Pb}}\right)_i + \frac{^{238}\text{U}}{^{204}\text{Pb}} (e^{\lambda T} - e^{\lambda t})$$

**Table for slope (m) for common lead isochrons:**

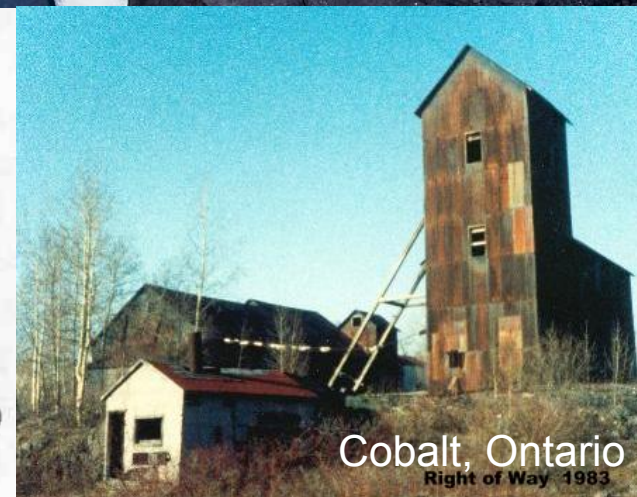
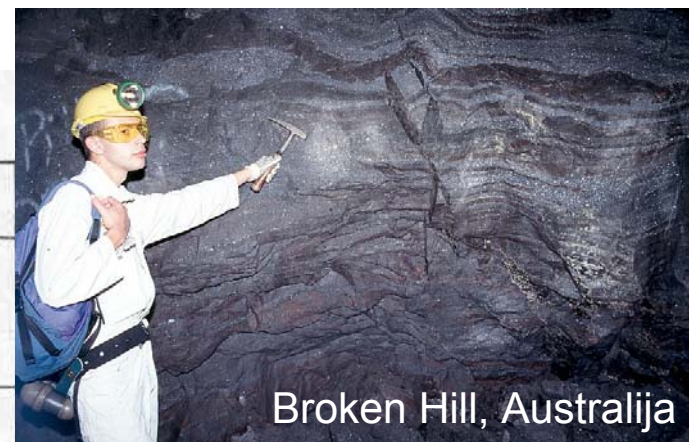
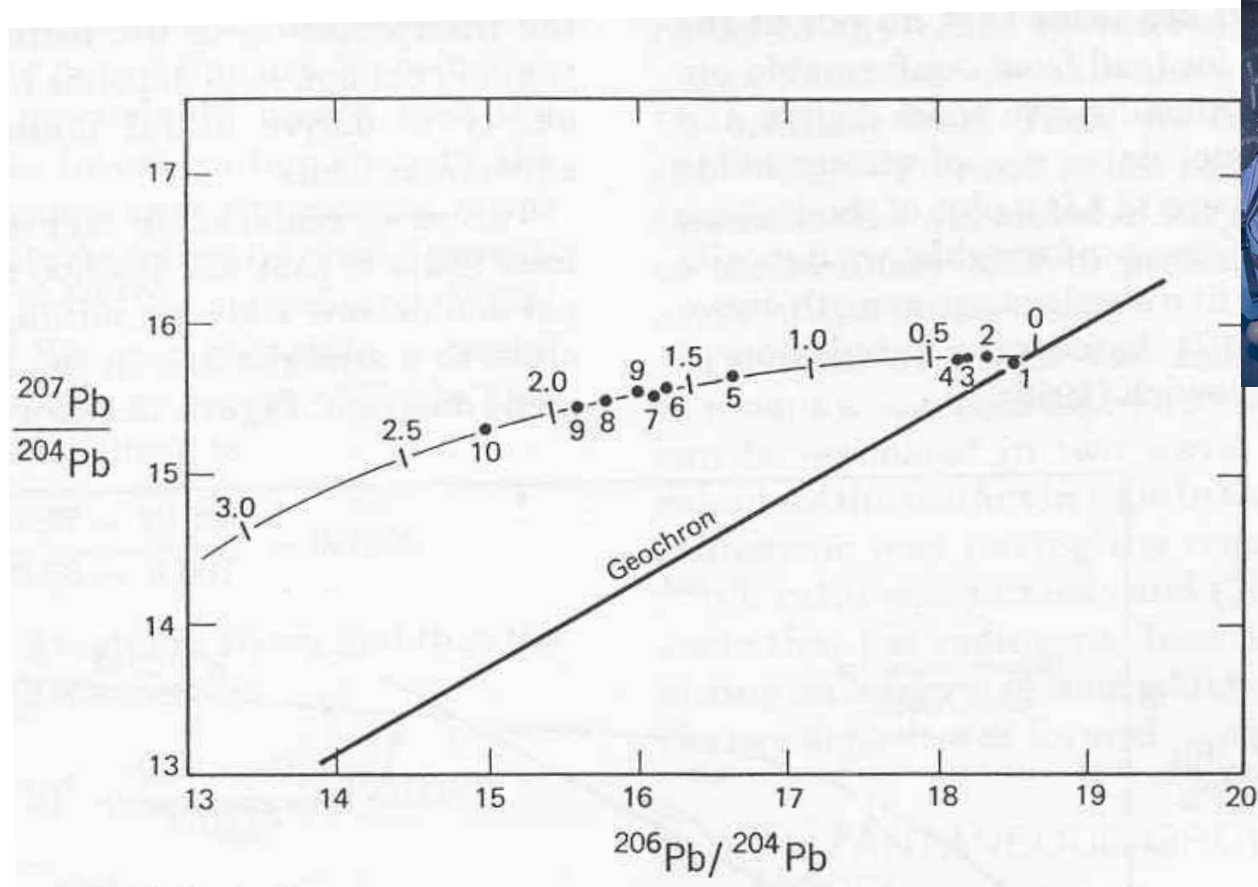
Age (yr)	207/206
0	0.618169
4.00E+08	0.636182
8.00E+08	0.655694
1.20E+09	0.676866
1.60E+09	0.699881
2.00E+09	0.724947
2.40E+09	0.752297
2.80E+09	0.782196
3.20E+09	0.814944
3.60E+09	0.850883
4.00E+09	0.8904
4.40E+09	0.933938
4.80E+09	0.981999



# Izotopni sastav olova iz konkordantnih ležišta sulfida

Prve analize ukazivale na podrijetlo olova iz Plašta

(ležišta Bathurst, Kanada; Cobar, Australija; Sullivan Mine, Kanada; Mt. Isa, Australija, Broken Hill, Australija, Cobalt, Ontario i dr.)



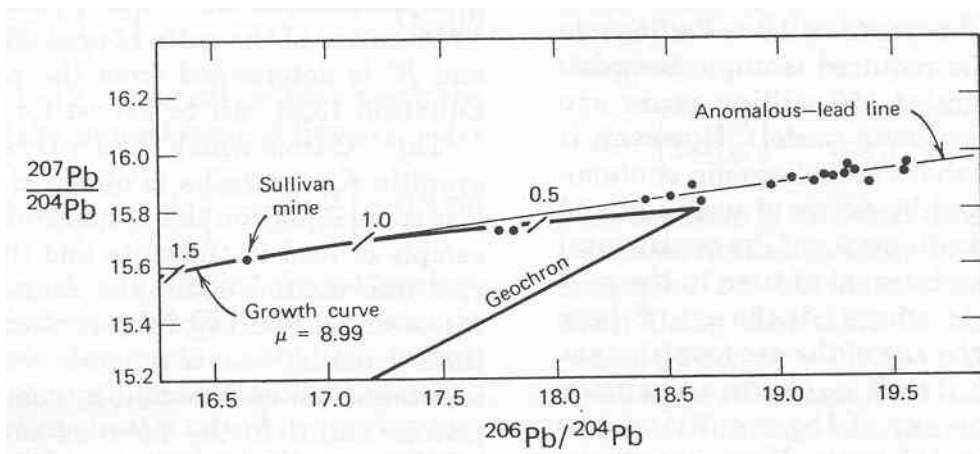
# «Anomalno» olovo

Anomalno olovo iz Kootenay Arca, British Columbia

Linija anomalnog olova ležišta Kootenay Arc, Kanada, leži izvan redovnog olova na liniji jednostupnog rasta.



**Galena**



Interpretacija:

1. **Trenutni rast** (malo vjerojatan)

Pb izvučeno iz rezervoara u vremenu  $t = 1.8 \times 10^9$  god. i zatim mješano s olovom karakterističnim za Sullivan rudno ležište  $1.33 \times 10^9$  izraslo jednostupnim rastom sa  $\mu = 9.0$

$$R = ({}^{207}\text{Pb}/{}^{206}\text{Pb})^* = 1/137.8 \cdot (e^{\lambda_2 t} / e^{\lambda_1 t})(\lambda_2 / \lambda_1)$$

$$t = 1/(\lambda_2 - \lambda_1) \ln [137.8 R \lambda_1 / \lambda_2]$$

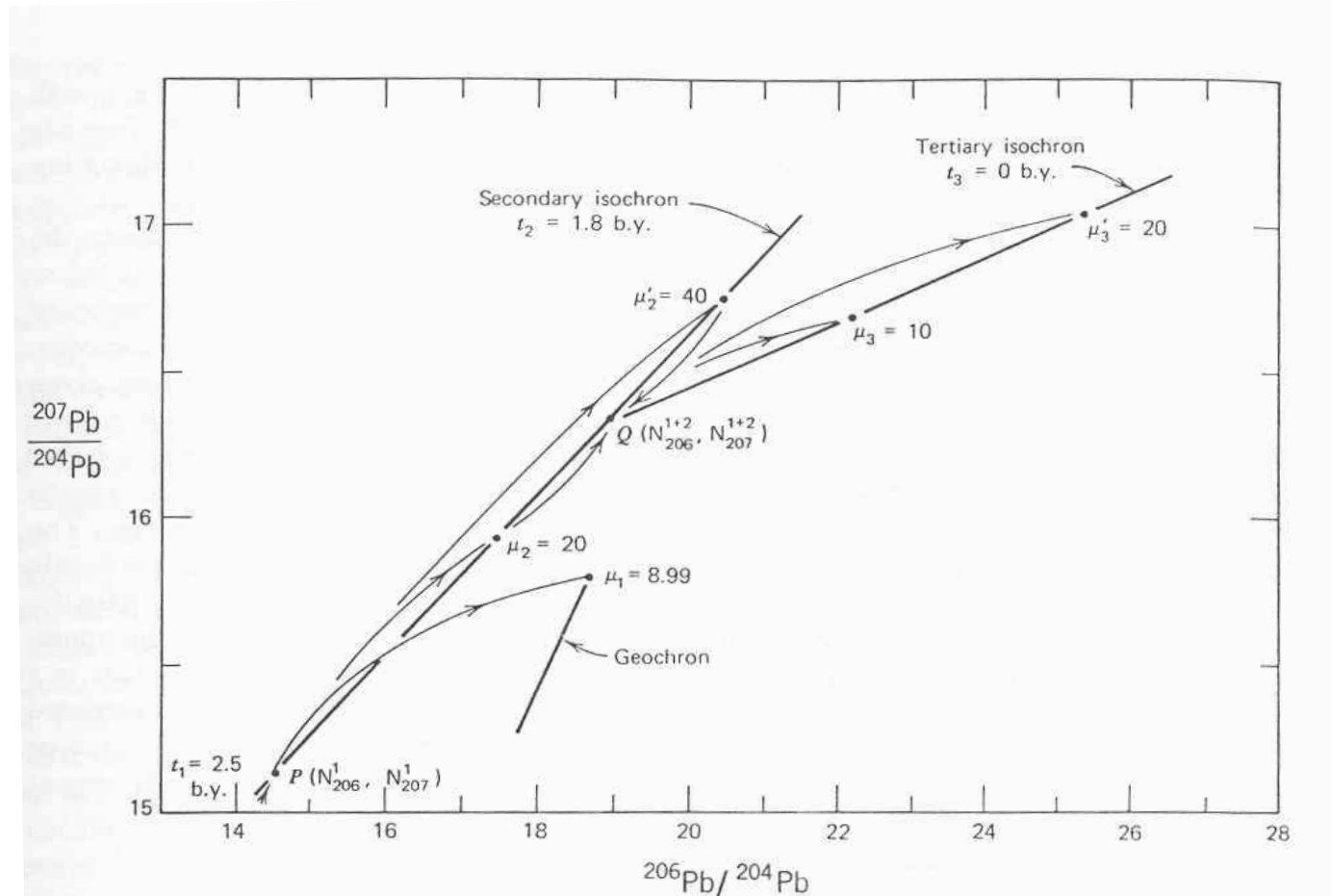
2. **Model kontinuiranog rasta**, Pb je izvučeno iz granitnih stijena koje su stare  $t_r$  a rudno ležište je nastalo u vrijeme  $t$ .

$$R = ({}^{206}\text{Pb}/{}^{204}\text{Pb})^* = 1/137.8 \cdot (e^{\lambda_{tr} t_r} - e^{\lambda t}) / (e^{\lambda_{tr} t_r} - e^{\lambda t})$$

# Metoda «zajedničkog» olova

## Common lead model

### Interpretacija više-stupnog olova



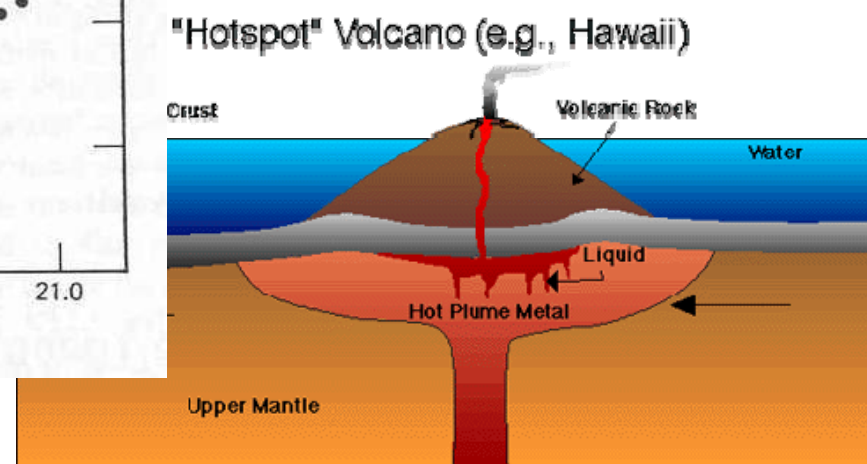
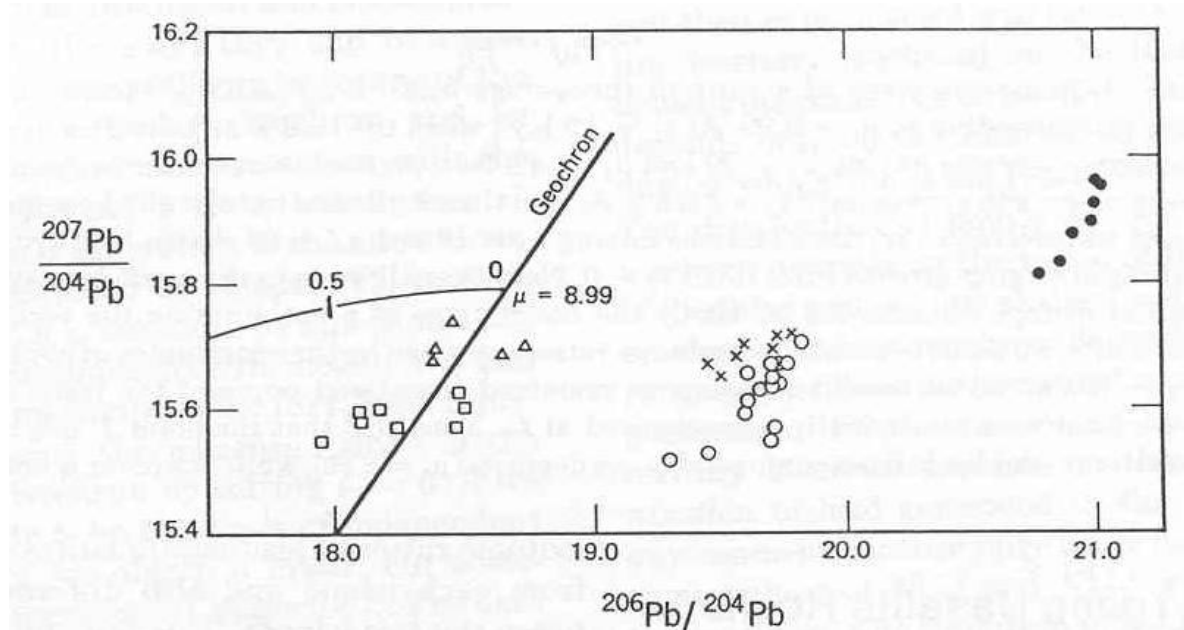
### Tri-stupanjsko olovo

Izotopska evolucija olova u tri stupnja (premještaj iz prvog rezearvoara u drugi i treći s različitim  $\mu$  vrijednostima ( $^{238}\text{U}/^{204}\text{Pb}$ ))

# Metoda «zajedničkog» olova

## Common lead model

### «Anomalno» olovo Izotopni sastav olova u mladim vulkanskim stijenama



- × Ascension otoci, O Tenerife, Kanarski otoci,
- St. Helena otok, □ Hawajski otoci, Δ Gough otoci

Izotopni sastav olova mladih vulkanskih stijena na oceanskim otocima pokazuje anomalne vrijednosti. To je evidencija heterogenosti Plašta (U/Pb), izvora magme na oceanskim otocima. Podaci ukazuju na otvorenost sustava tijekom geološkog vremena, tj. više-stupni razvoj.

# U-Pb konkordija

## Zatvoren sustav



cirkon

Konkordia, linija konkordantnih vrijednosti  $^{206}\text{Pb}/^{238}\text{U}$  i  $^{207}\text{Pb}/^{235}\text{U}$

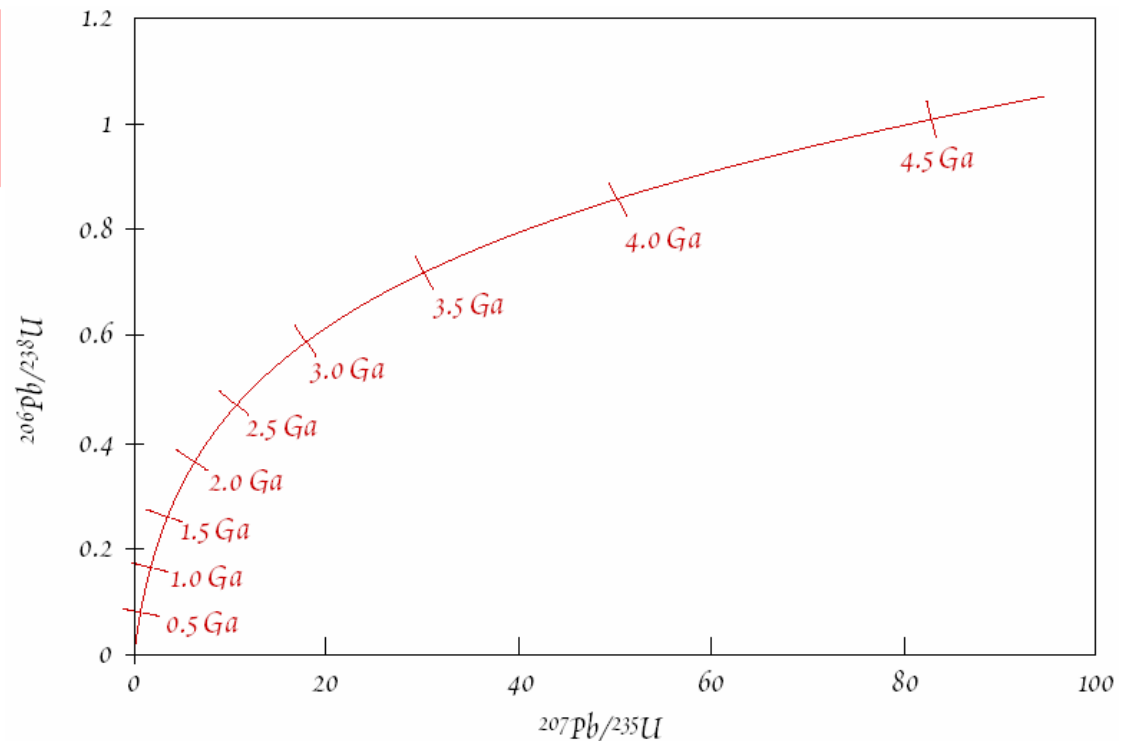
### Pretpostavke:

1. Kod  $t = 0$  (kristalizacija), oba kvocijenta = 0
2. Sustav se razvija neporemećen tako dugo dok ostaje zatvoren za U i Pb.
3. Oba kvocijenta mogu poslužiti za računanje starosti

$$\frac{^{206}\text{Pb}}{^{204}\text{Pb}} = \left( \frac{^{206}\text{Pb}}{^{204}\text{Pb}} \right)_i + \frac{^{238}\text{U}}{^{204}\text{Pb}} (e^{\lambda t} - 1)$$

$$\frac{^{206}\text{Pb}^*}{^{238}\text{U}} = (e^{\lambda_8 t} - 1)$$

$$\frac{^{207}\text{Pb}^*}{^{235}\text{U}} = (e^{\lambda_5 t} - 1)$$



# U-Pb diskordija

## Otvoren sustav

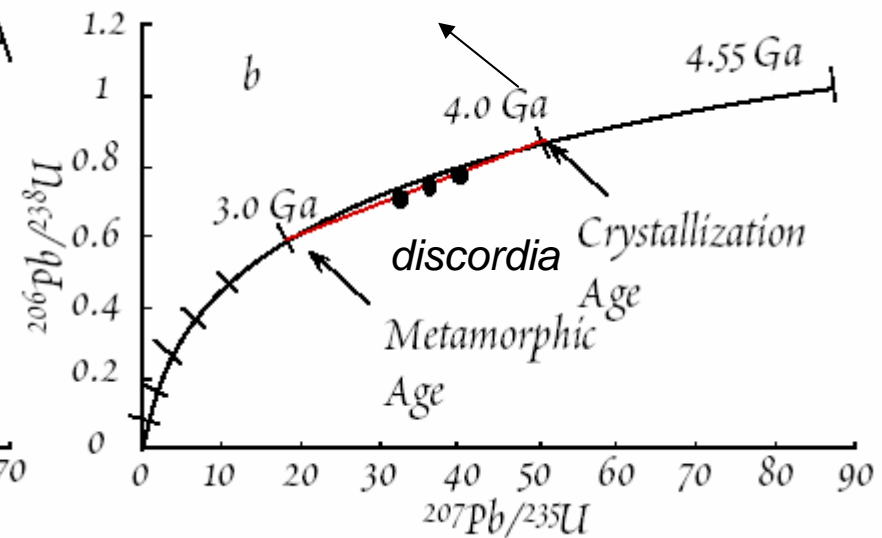
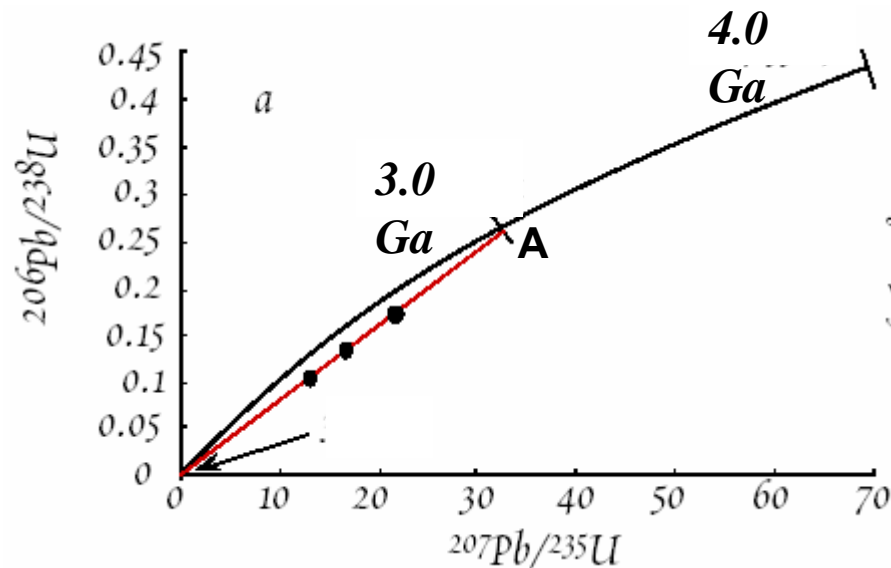
### Pitanje:

Što ako se tijekom metamorfizma Pb gubi (vrlo često)?

### Diskordija za cirkon nastao 4.0 Ga a doživio metamorfizam prije 3 Ga

Gubitak Pb prije 3 Ga (3 milijarde godina) pomiče uzorke iz točke A prema ishodištu. Potpuni gubitak pomaknuo bi uzorke u ishodište, (otvoren sustav, reset).

Ako uzorak ostaje zatvoren od trenutka metamorfizma do sadašnjice, uzorci prate diskordiju (pravac) između 3 Ga (metamorfizam) i 4 Ga (kristalizacija).



Diskordija definirana izmijenjenim uzorcima presječi će Konkordiju u vremenu kristalizacije i vremenu metamorfizma.

# U-Pb diskordija

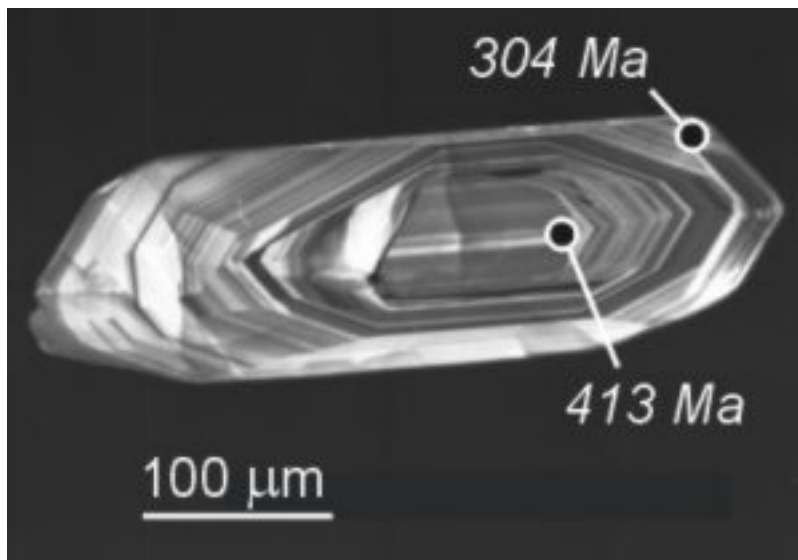
## Otvoren sustav



### Pitanje:

Što ako uzorak prolazi kroz nekoliko metamorfizama (višestruki metamorfizam)?

Linija diskordija postaje zakrivljena, kontinuirani difuzioni gubitak Pb iz U bogatih minerala. Za više struko metamorfoziranje ne koristimo metodu Konkordije.



### Pitanje:

Kako bi izgledala diskordija ako je 413 Ma godina stari cirkona, djelomično «resetiran» (izmjenjen) i uklopljen u 304 Ma staru taljevinu?

a) ako se izotopi olova i urana pri tome homogeniziraju?

b) ako nova taljevina proizvodi cirkonski priraštajni omotač?

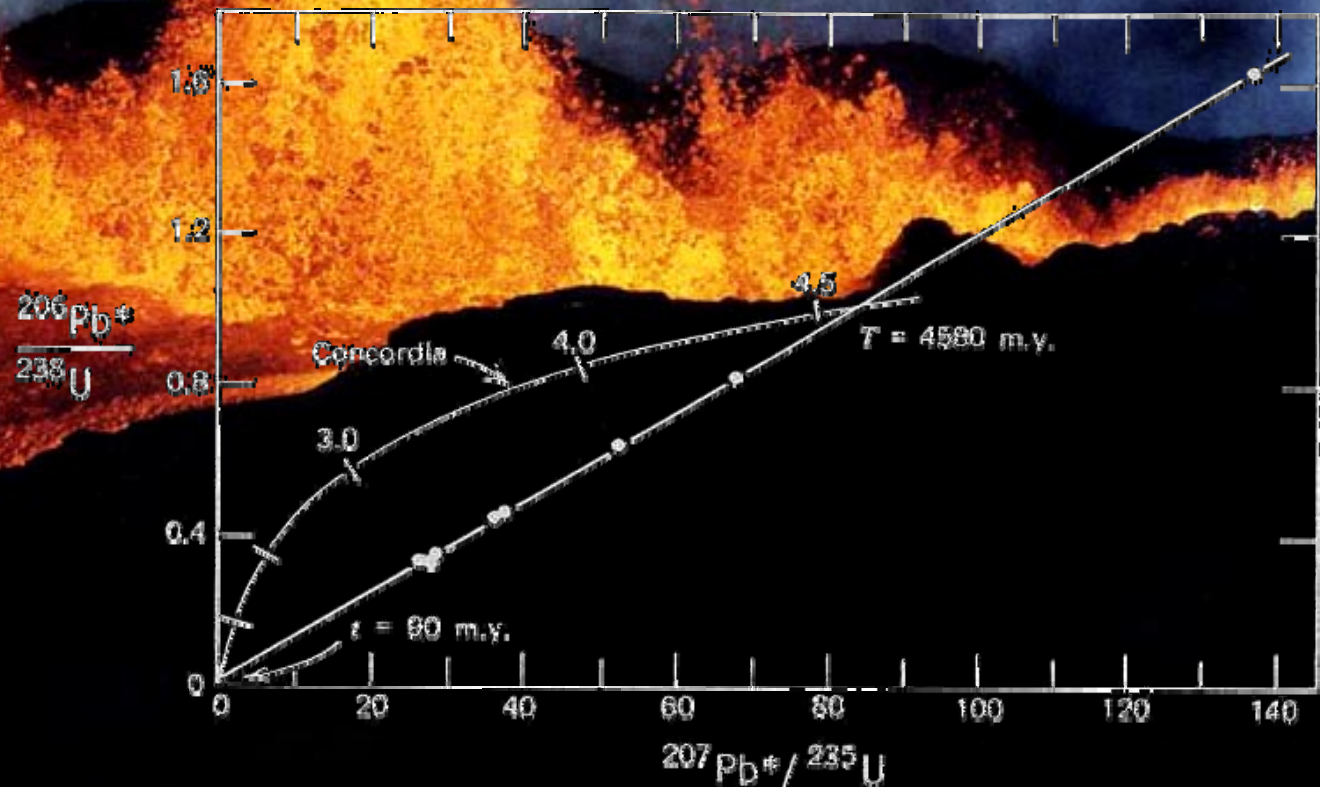
# U-Pb diskordija

Otvoren sustav

Pitanje:

Kako bi izgledala diskordija ako se tijekom kemijskog trošenja gubio uran prije 4 Ga?

Izotopni razvoj olova u vulkanskim stijenama Hawaiia. Konkordija upućuje na starost rezervoara olova 4580 Ma a presjecište u donjem dijelu konkordije na «nedavnu» heterogenizaciju Plašta iz kojeg dolazi magma (90 Ma).



Hawaii

# U-Pb diskordija

## Otvoren sustav

MORB bazalti daju starost Plašta diskordijom 4480 do 4580 Ma. Za Tihi ocean heterogenost nastupa između 0 i 220 Ma, a za Atlanski ocean taj se događaj zbio prije 1230 Ma.

# Pb-izotopi

## Sansko-unski paleozoik

- Doe-Stacy model rasta (Brdo/Adamuša) pokazuje vrijednost od oko **240 Ma** (PALINKAŠ, 1985)

