Geochemical dating of a Swiss freshwater limestone cave using $^{230}Th/^{234}U$ ingrow and ^{226}Ra-excess decay chronometry

Jost Eikenberg, Maya Jäggi

Division for Radiation Protection and Safety

Paul Scherrer Institute, CH-5232 Villigen

Overview / Topics

- Presentation of a radiochemical method for simultaneous determination of ^{226}Ra+^{228}Ra followed by TDCR-measurement and optimized alpha/beta-separation

- Application of the chronometers ^{230}Th/^{234}U and ^{226}Ra for dating sedimentary systems

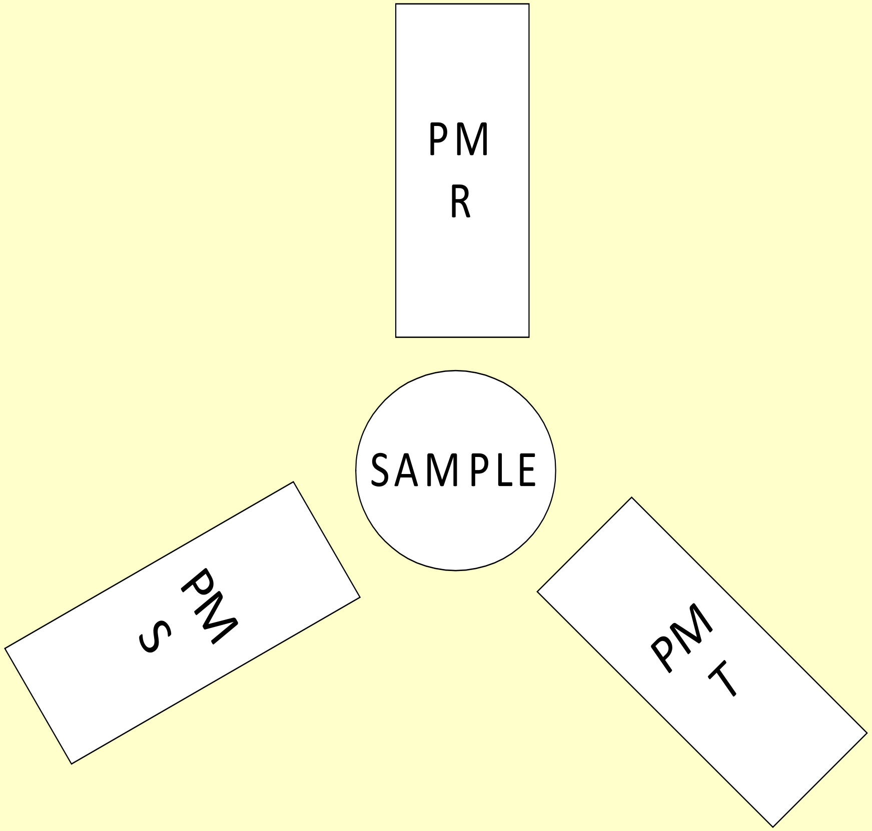
relevant isotopes for quaternary limestone dating

radionuclide	**analytical technique**
^{234}U, (^{235}U), ^{238}U, ^{230}Th, ^{232}Th	U/TEVA separation, electro-deposition, α-spectrometry
^{226}Ra, ^{228}Ra	filtration (RadDisc), OptiPhase Hisafe3 cocktail, LSC
^{210}Po	spontaneous deposition on silver disc, α-spectrometry

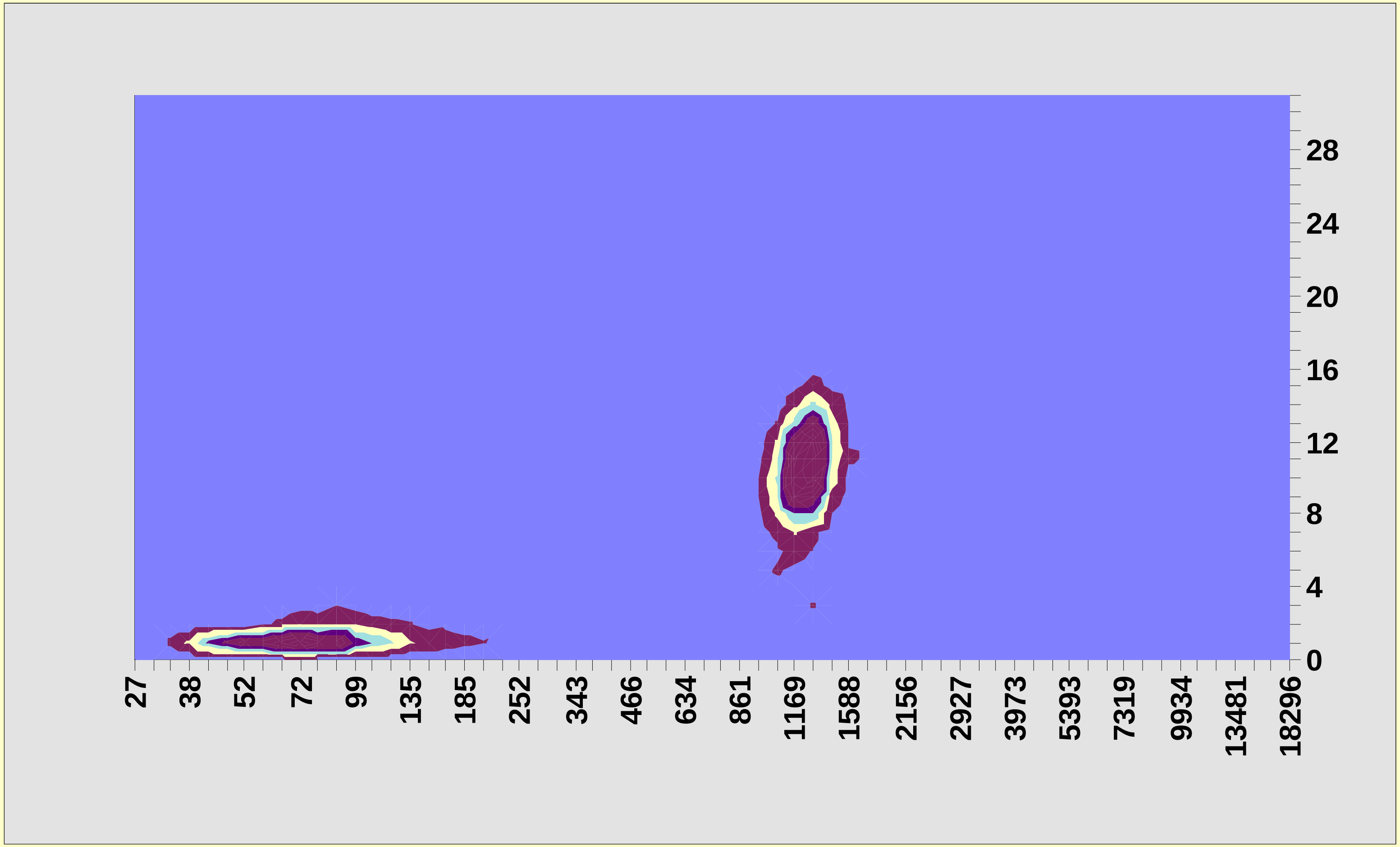
Method implementation: low level determination of ^{226}Ra in sediments (limestone)

- Sample dissolution $CaCO_3$ in 1 mol/liter HCl, evaporation, dilution with distilled water
- Filtration of the sample through 3 Empore RadDisc (Mn-oxide impregnated) membrane
- Elution of Ra with alkaline Na-EDTA solution
- Measuring via LSC with optimized α/β-discrimination

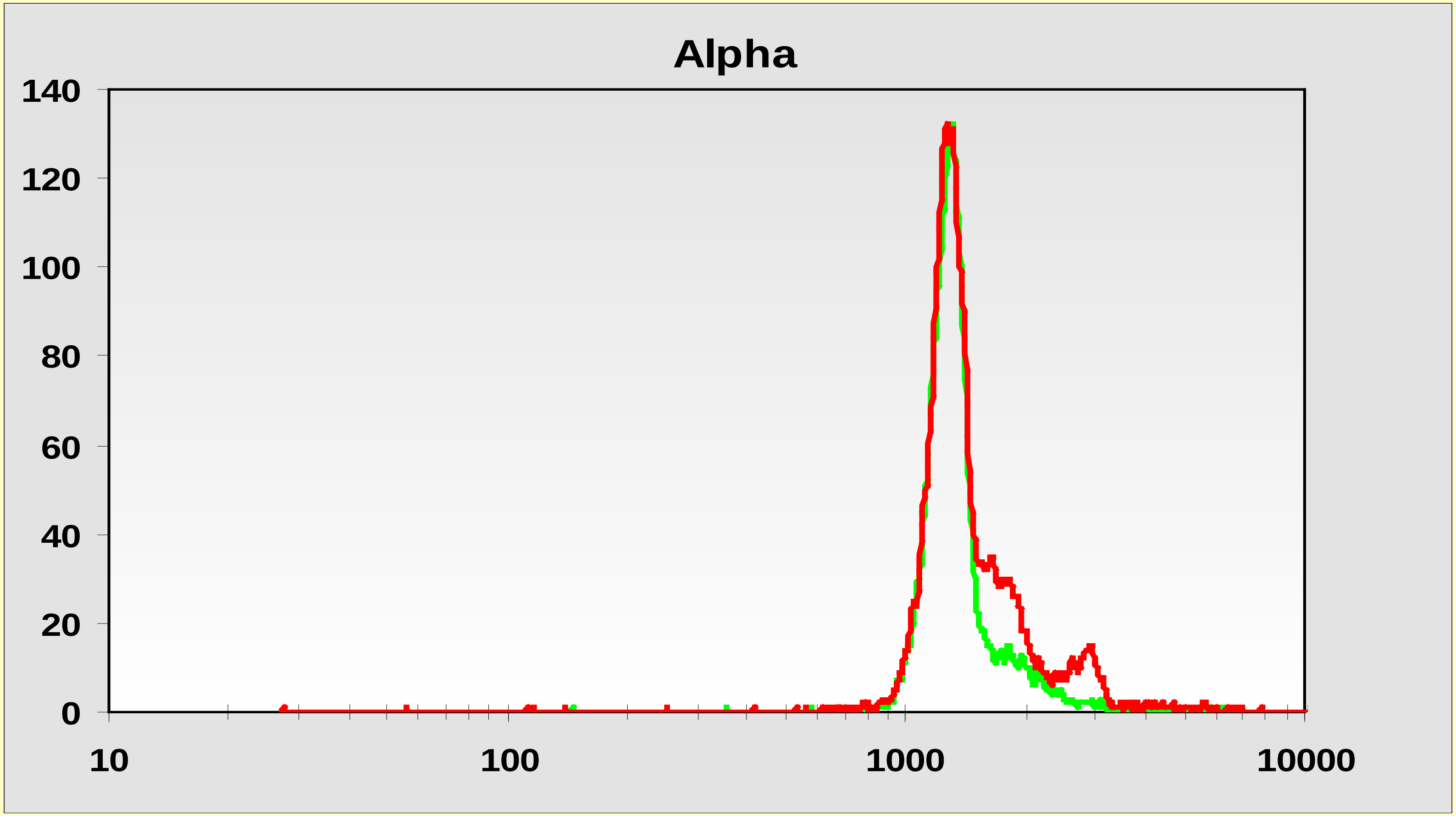
The triple coincidence to double coincidence ratio (TDCR) counting technique



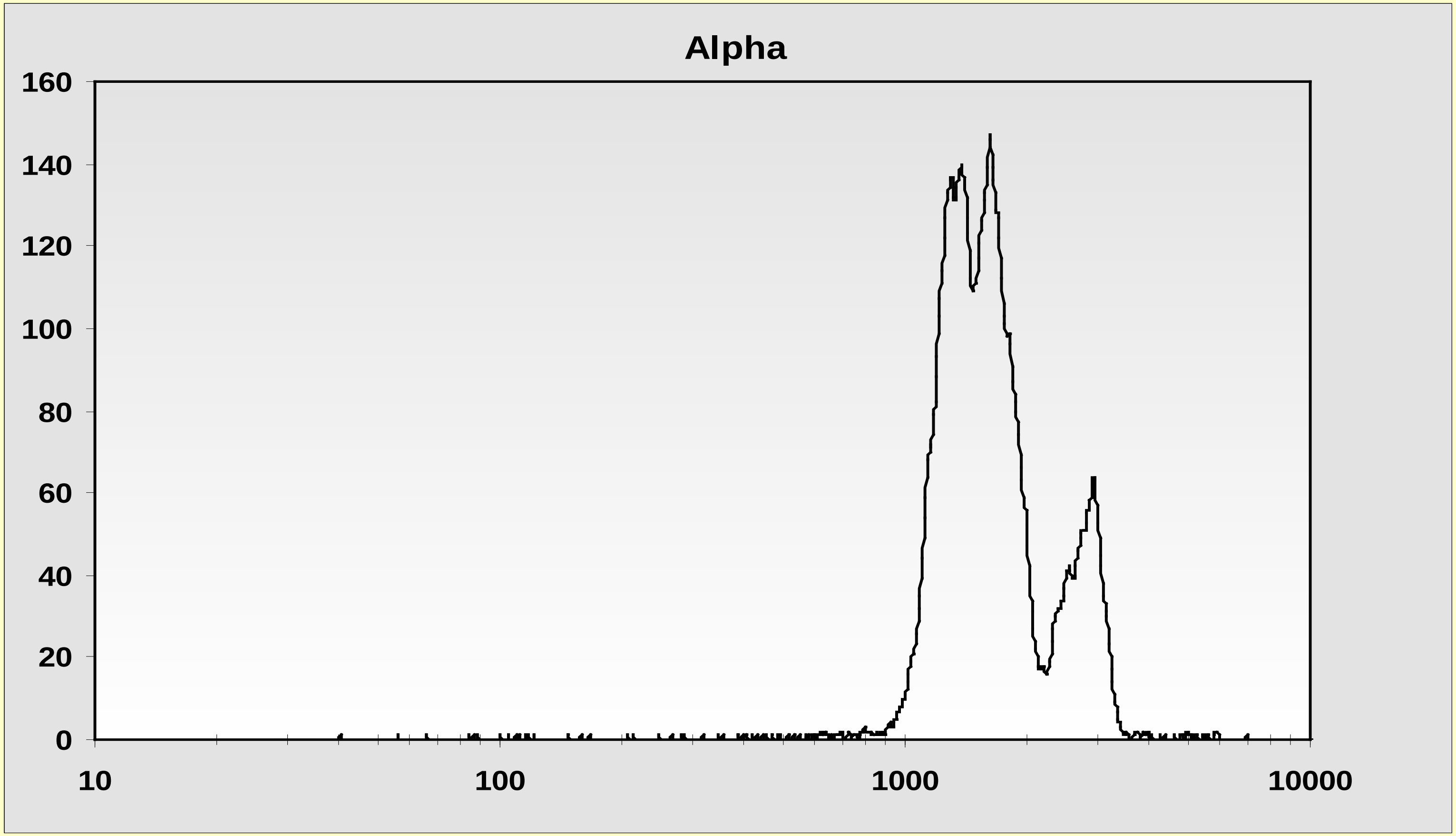
Pulse Length Index (PLI) discrimination with HIDEX SL 300



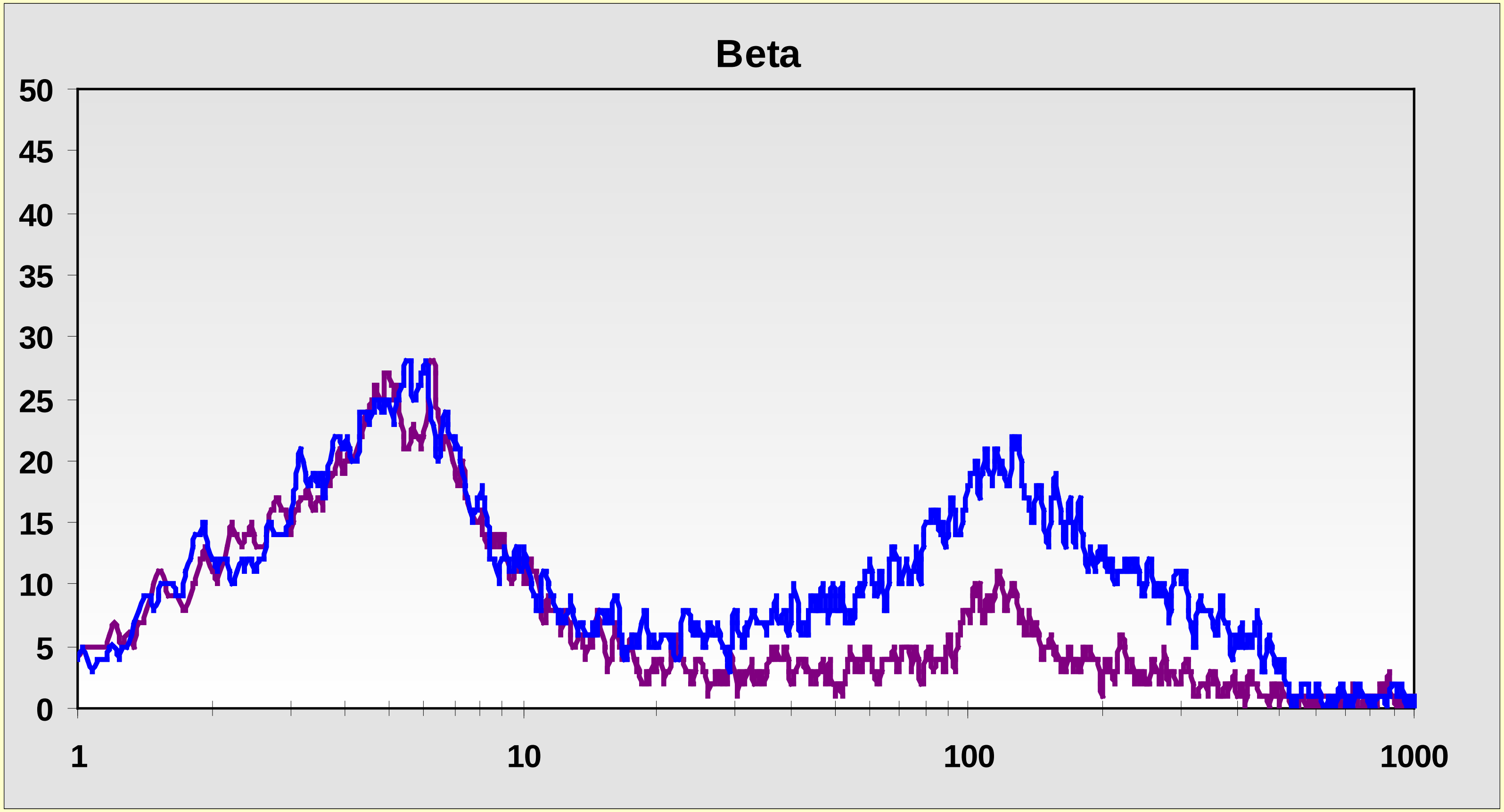
α-spectrum of ^{226}Ra with ingrowing daughters 2 h and 8 h after separation using HIDEX 300 SL LSC



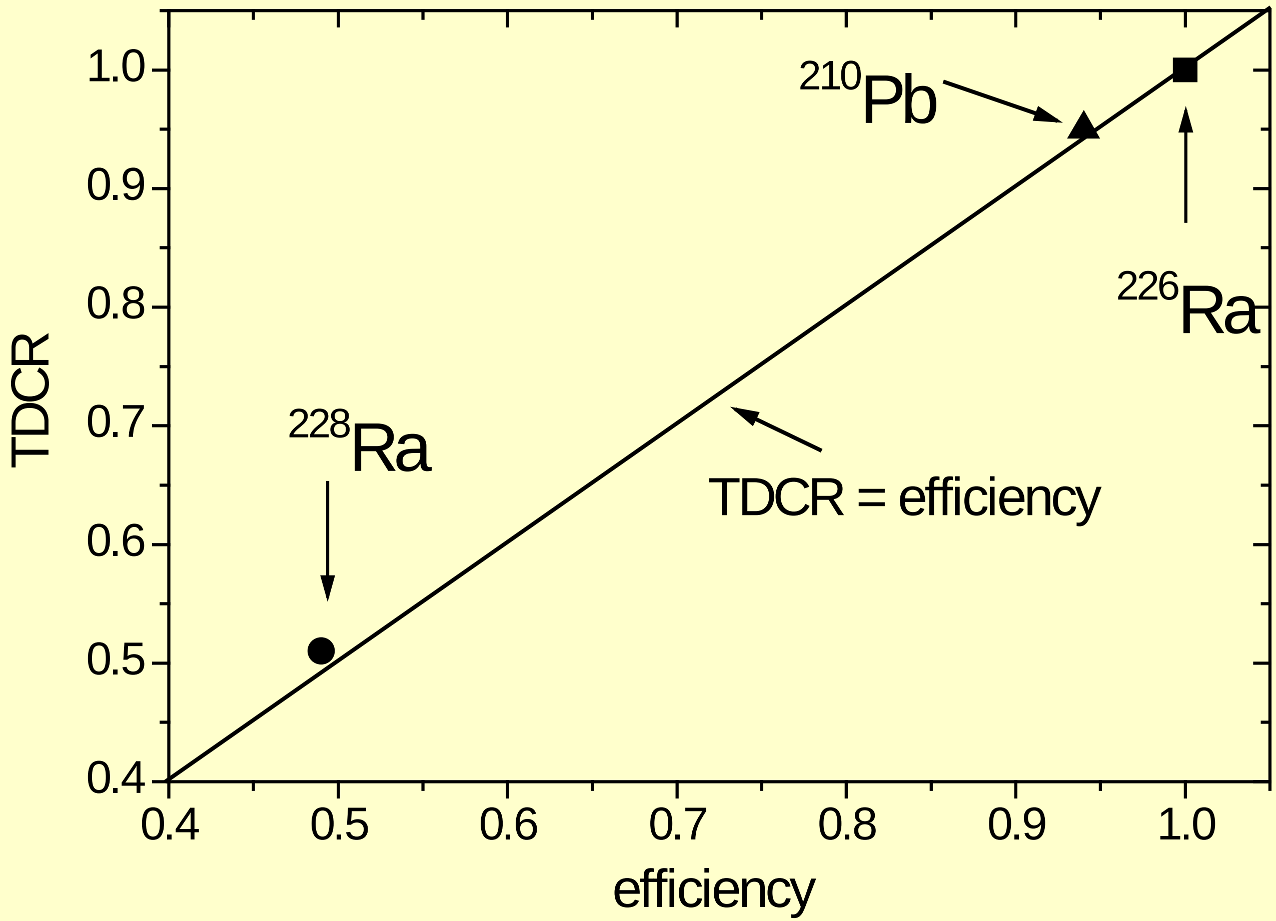
α-spectrum of ^{226}Ra with ingrowing daughters obtained 6 days after separation



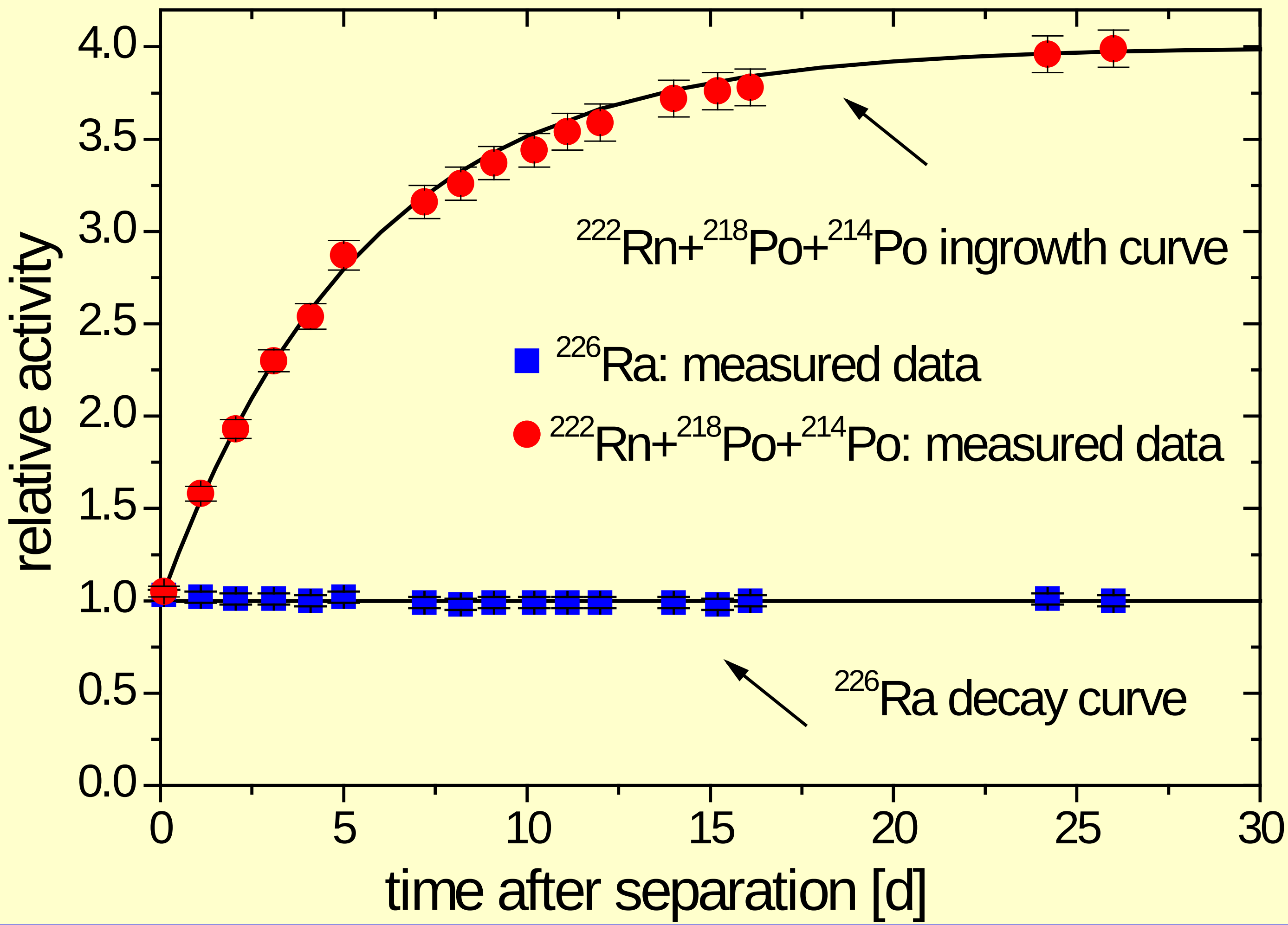
β-spectrum of ^{228}Ra with ingrowing ^{228}Ac 1 h and 8 h after separation using HIDEX 300 SL LSC

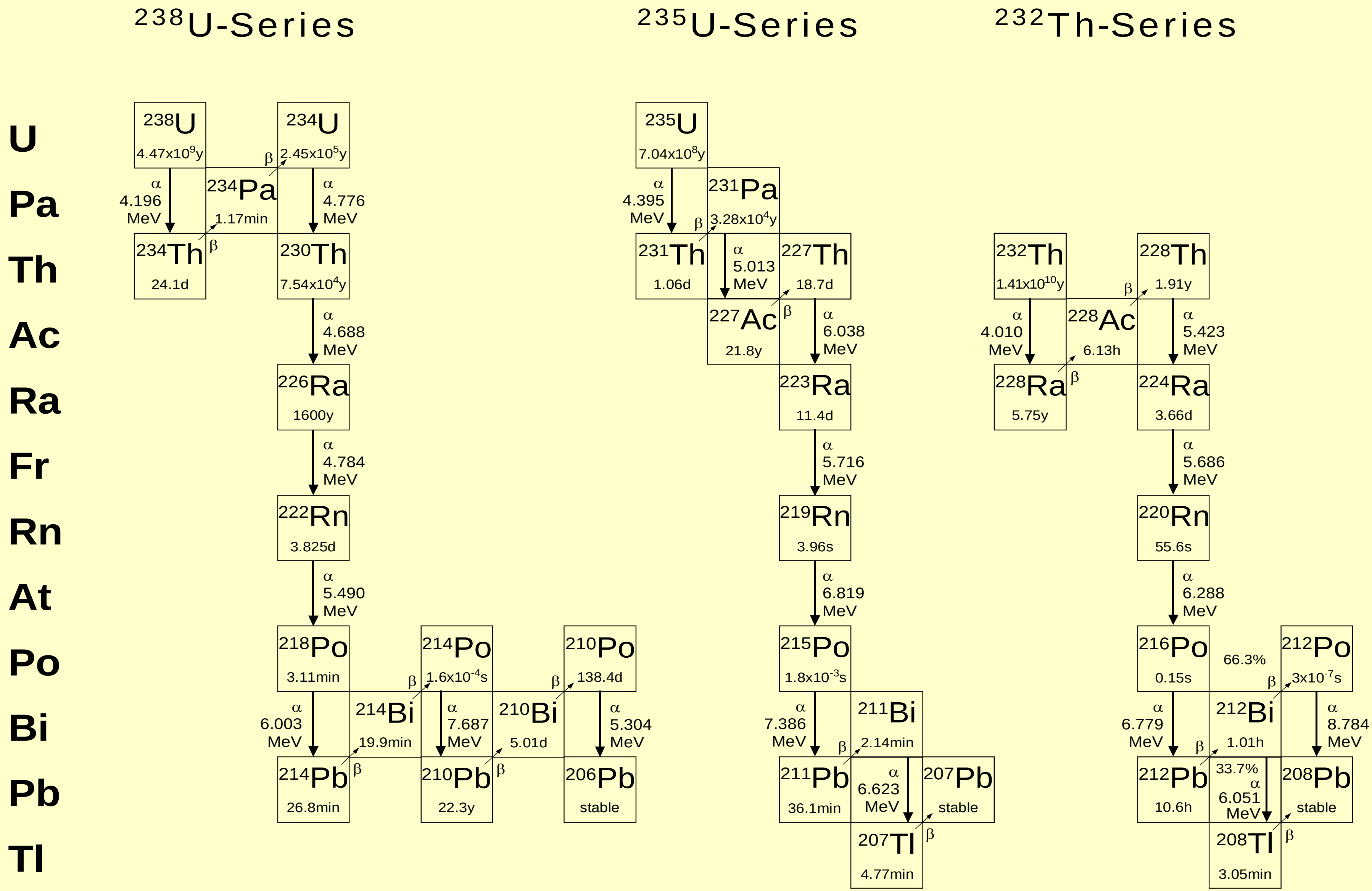


TDCR vs. Efficiency using high purity radionuclide standard solutions



Comparison of measured ^{226}Ra and the progeny isotopes ^{222}Rn, ^{218}Po and ^{214}Po with calculated decay/ingrowth curves

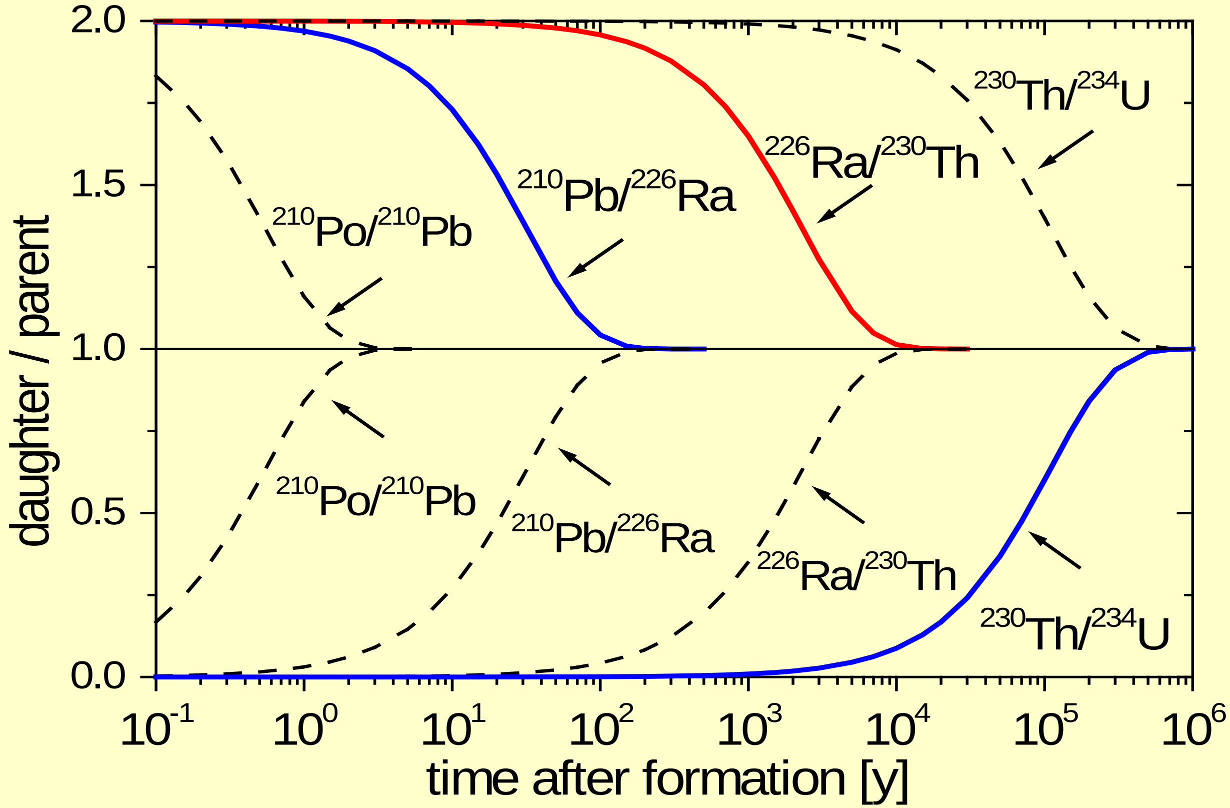




238U-Series
235U-Series
232Th-Series
U
Pa
Th
Ac
Ra
Fr
Rn
At
Po
Bi
Pb
Tl
238U 4.47x10^9y
α 4.196 MeV
234Th 24.1d
β
234Pa 1.17min
β
234U 2.45x10^5y
α 4.776 MeV
230Th 7.54x10^4y
α 4.688 MeV
226Ra 1600y
α 4.784 MeV
222Rn 3.825d
α 5.490 MeV
218Po 3.11min
α 6.003 MeV
214Pb 26.8min
β
214Bi 19.9min
β
214Po 1.6x10^-4s
α 7.687 MeV
210Pb 22.3y
β
210Bi 5.01d
β
210Po 138.4d
α 5.304 MeV
206Pb stable
235U 7.04x10^8y
α 4.395 MeV
231Th 1.06d
β
231Pa 3.28x10^4y
α 5.013 MeV
227Ac 21.8y
β
227Th 18.7d
α 6.038 MeV
223Ra 11.4d
α 5.716 MeV
219Rn 3.96s
α 6.819 MeV
215Po 1.8x10^-3s
α 7.386 MeV
211Pb 36.1min
β
211Bi 2.14min
α 6.623 MeV
207Tl 4.77min
β
207Pb stable
232Th 1.41x10^10y
α 4.010 MeV
228Ra 5.75y
β
228Ac 6.13h
β
228Th 1.91y
α 5.423 MeV
224Ra 3.66d
α 5.686 MeV
220Rn 55.6s
α 6.288 MeV
216Po 0.15s
α 6.779 MeV
212Pb 10.6h
β
212Bi 1.01h
66.3%
β
212Po 3x10^-7s
α 8.784 MeV
33.7%
α 6.051 MeV
208Tl 3.05min
β
208Pb stable

Challange for the isotope geochemist: closing the gap between the established ^{210}Pb and ^{230}Th/^{234}U chronometers

$$^{238}U \rightarrow {}^{234}U \rightarrow {}^{230}Th \rightarrow {}^{226}Ra\left({}^{222}Rn\right) \rightarrow {}^{210}Pb\left({}^{210}Po\right)$$



Principles of U series dating: 1. ^{230}Th/^{234}U/^{238}U

$$^{230}Th(t) = {}^{230}Th(0)\cdot e^{-\lambda_{230}t} + {}^{234}U(0)\cdot(e^{-\lambda_{234}t} - e^{-\lambda_{230}t})$$

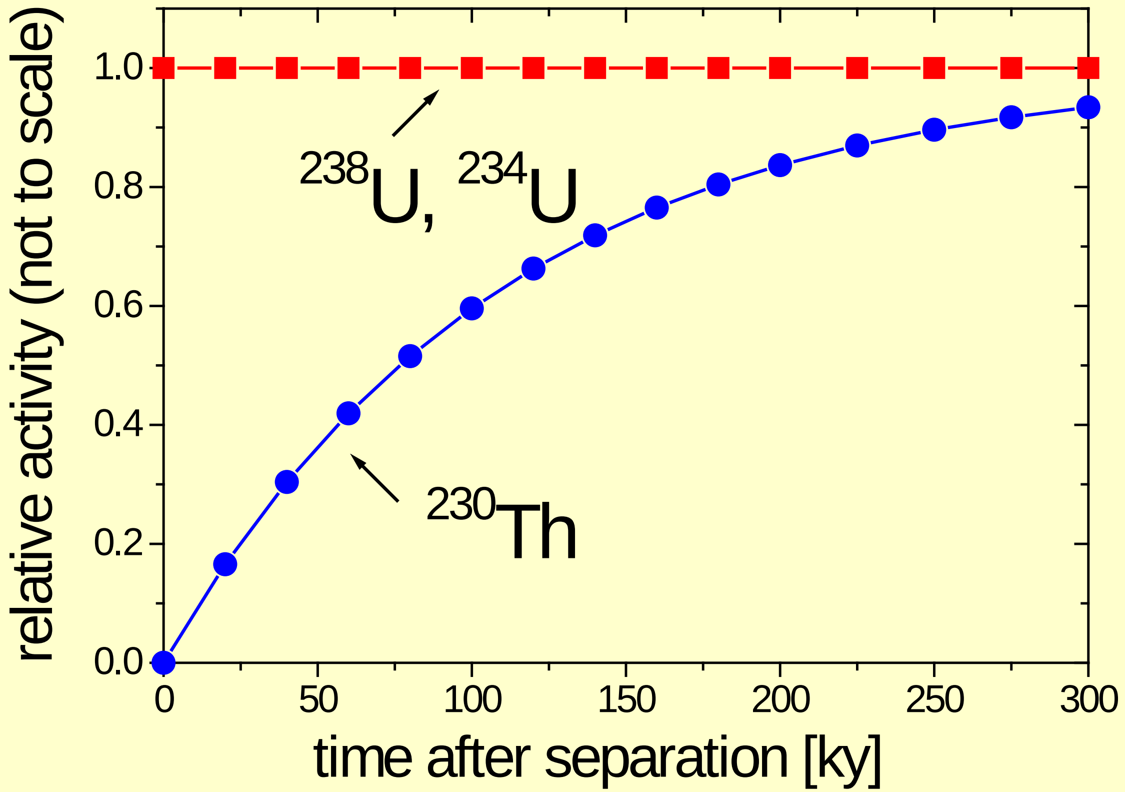
$$^{230}Th(t) = {}^{234}U(0)\cdot(e^{-\lambda_{234}t} - e^{-\lambda_{230}t})$$

$$^{234}U(t) = {}^{234}U(0)\cdot e^{-\lambda_{238}t}$$

$$^{230}Th(t) = {}^{234}U(0)\cdot\left(1 - e^{-\lambda_{230}t}\right)$$

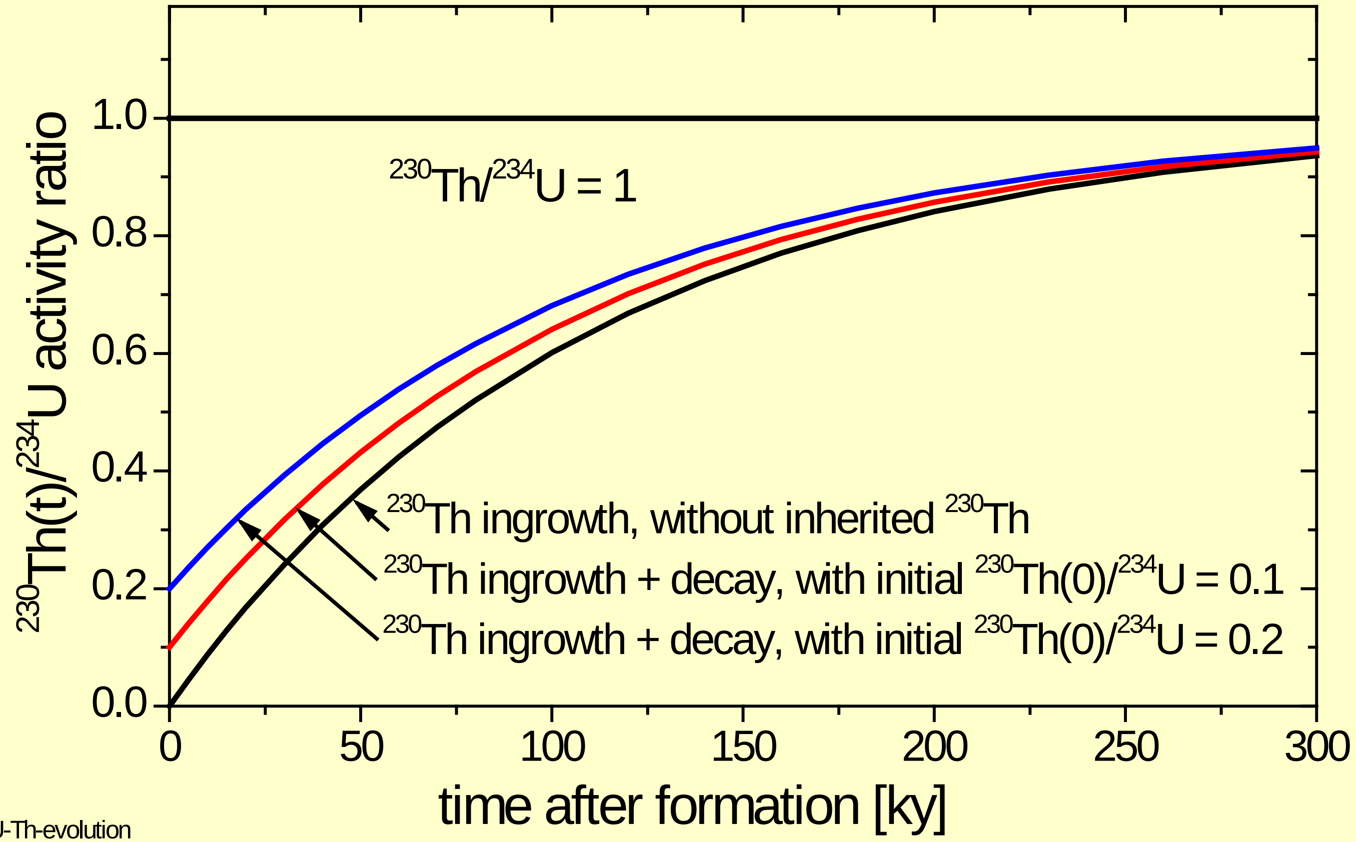
Principles of U series dating: 1. $^{230}Th/^{234}U/^{238}U$

$$^{234}U(0) = {}^{238}U(0) = {}^{238}U \qquad {}^{230}Th(t) = {}^{234}U(0) \cdot \left(1 - e^{-\lambda_{230} t}\right)$$



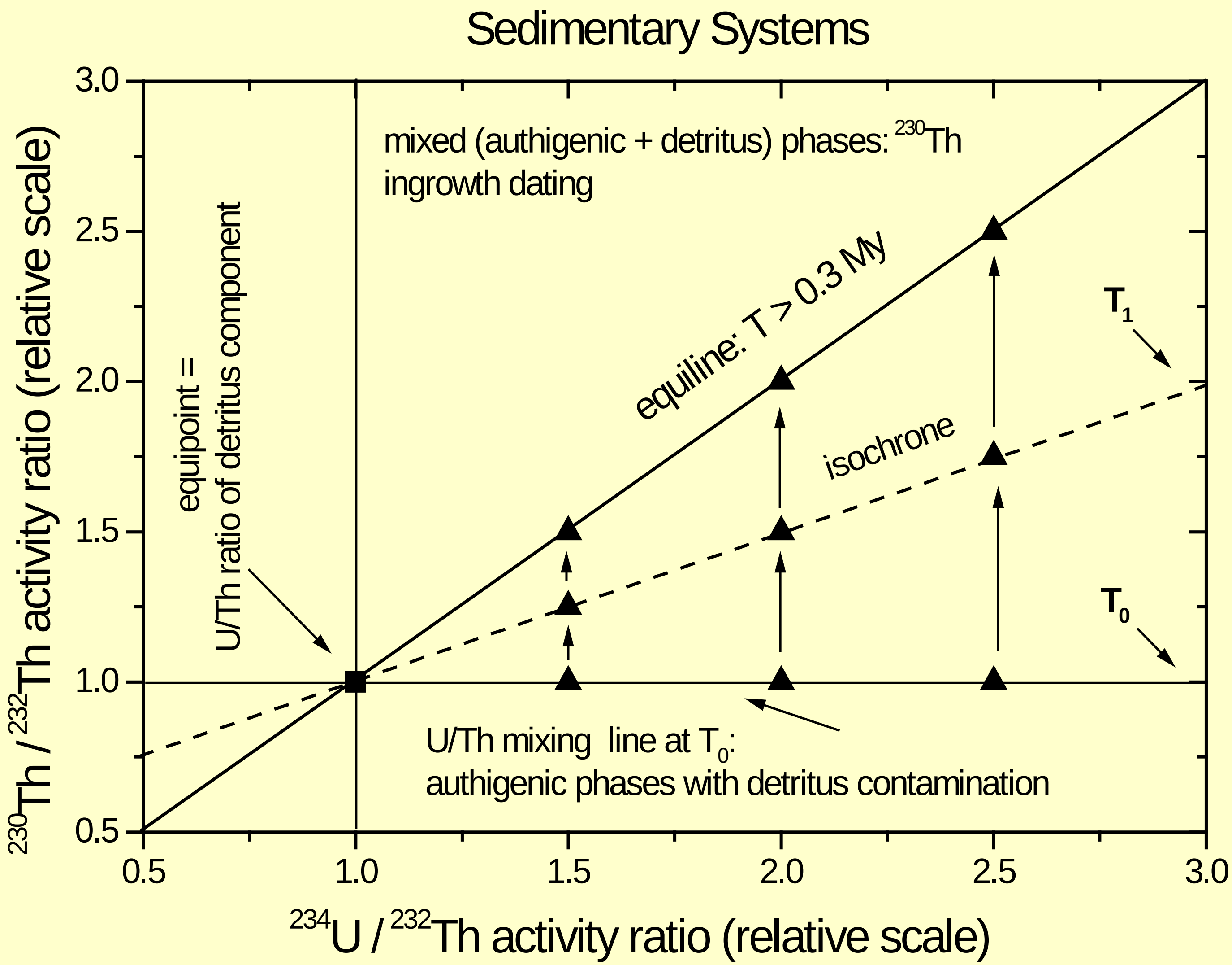
Problem 1: inherited ^{230}Th, wrong age calculation

$$^{230}Th(t) = {}^{234}U(0)\cdot\left(1-e^{-\lambda_{230}t}\right)+{}^{230}Th(0)\cdot e^{-\lambda_{230}t}$$

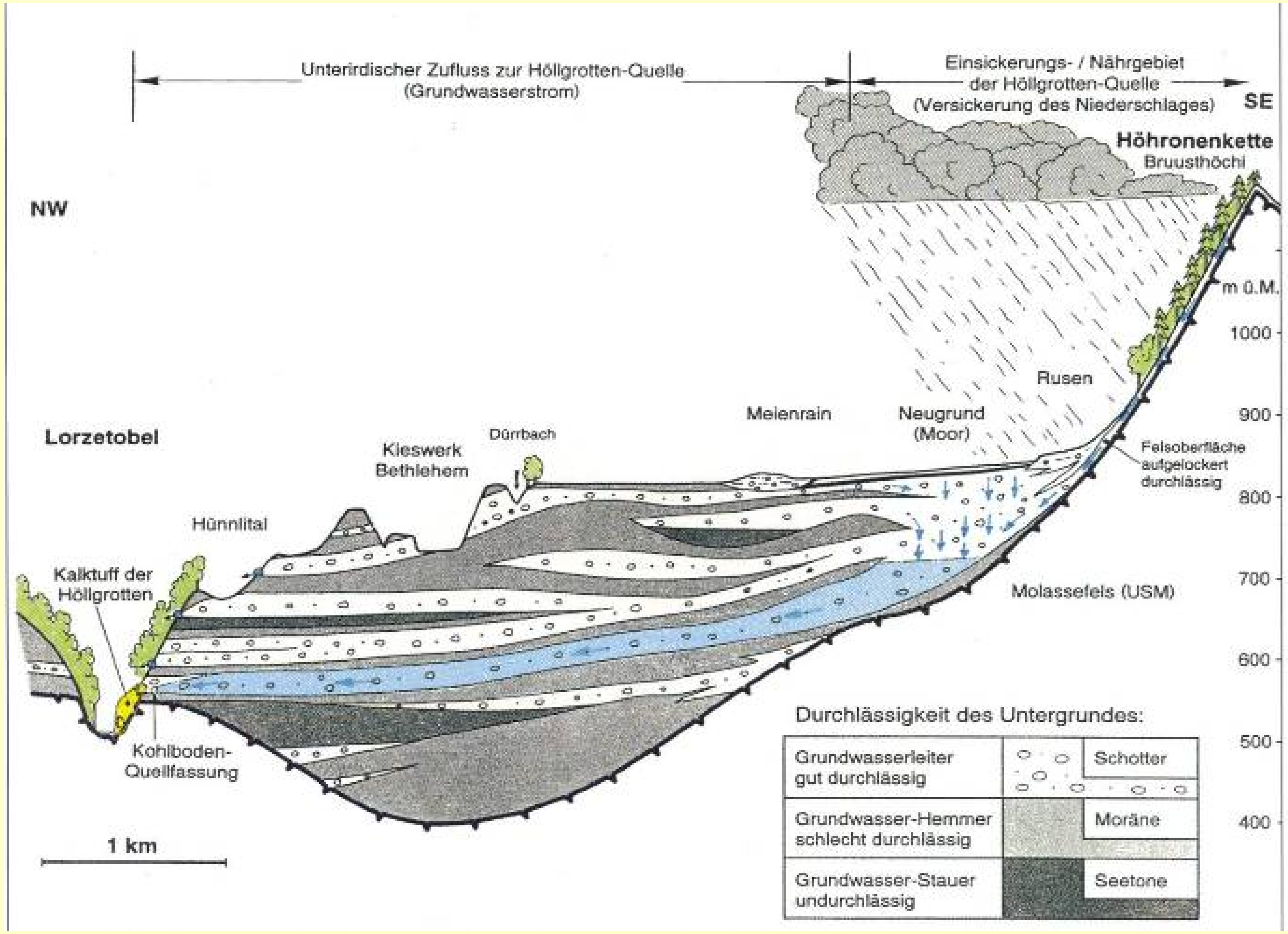


U-Th-evolution

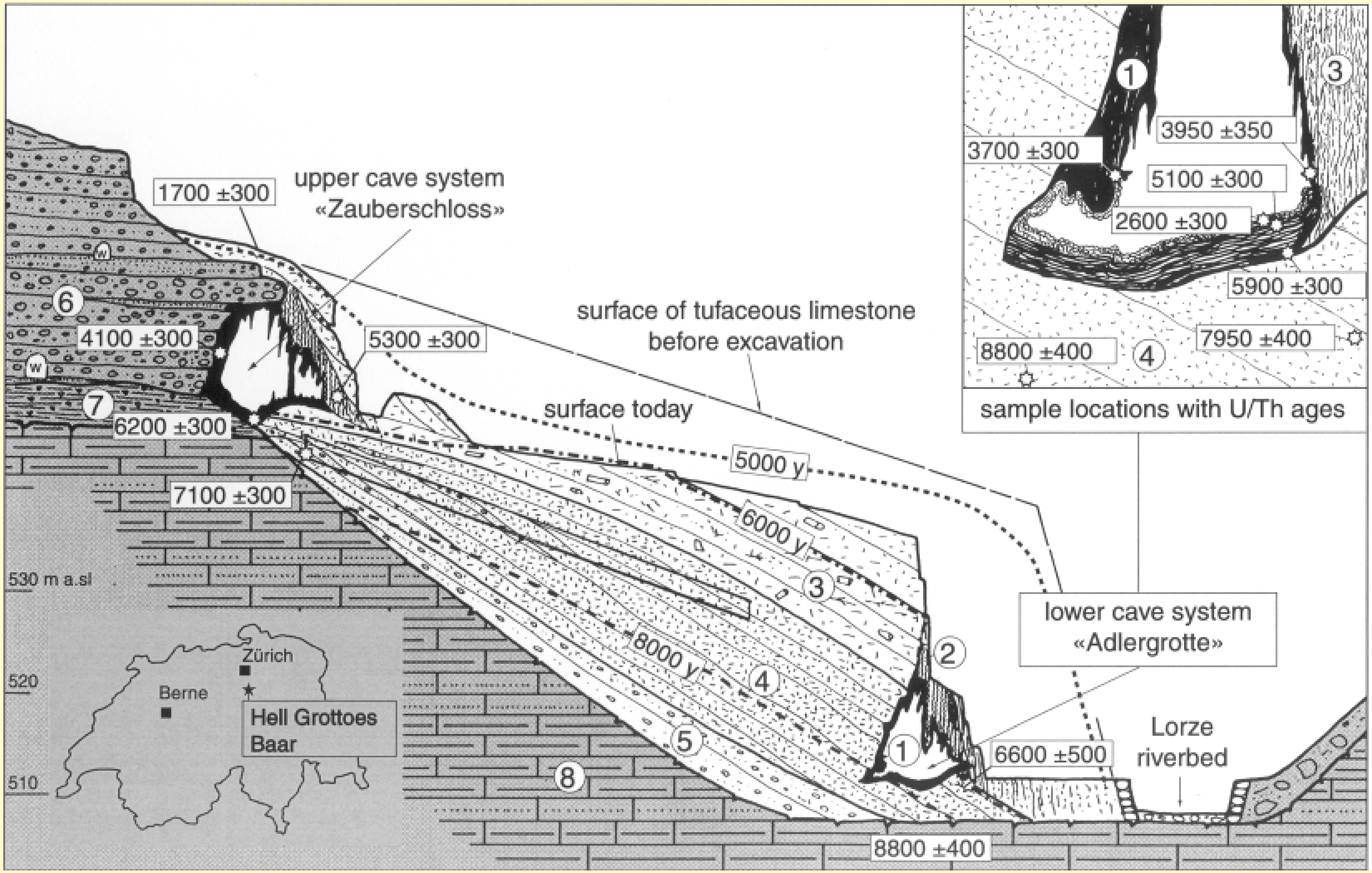
U-series application with U-Th isochrones in sedimentology



Geological section of the aquifer / recharge area of hell grottoes springs



Travertine dating via $^{226}Ra_{ex}/^{234}U$ and $^{230}Th/^{234}U$



View into the cave system

Travertine precipitation: thermodynamic background

$$\prec H_2CO \succ + O_2 \rightarrow CO_2 + H_2O$$

$$CO_2 + H_2O \rightarrow H_2CO_3 \rightarrow H^+ + HCO_3^-$$

$$CaCO_3 + H^+ + HCO_3^- \leftrightarrow Ca^{2+} + 2HCO_3^-$$

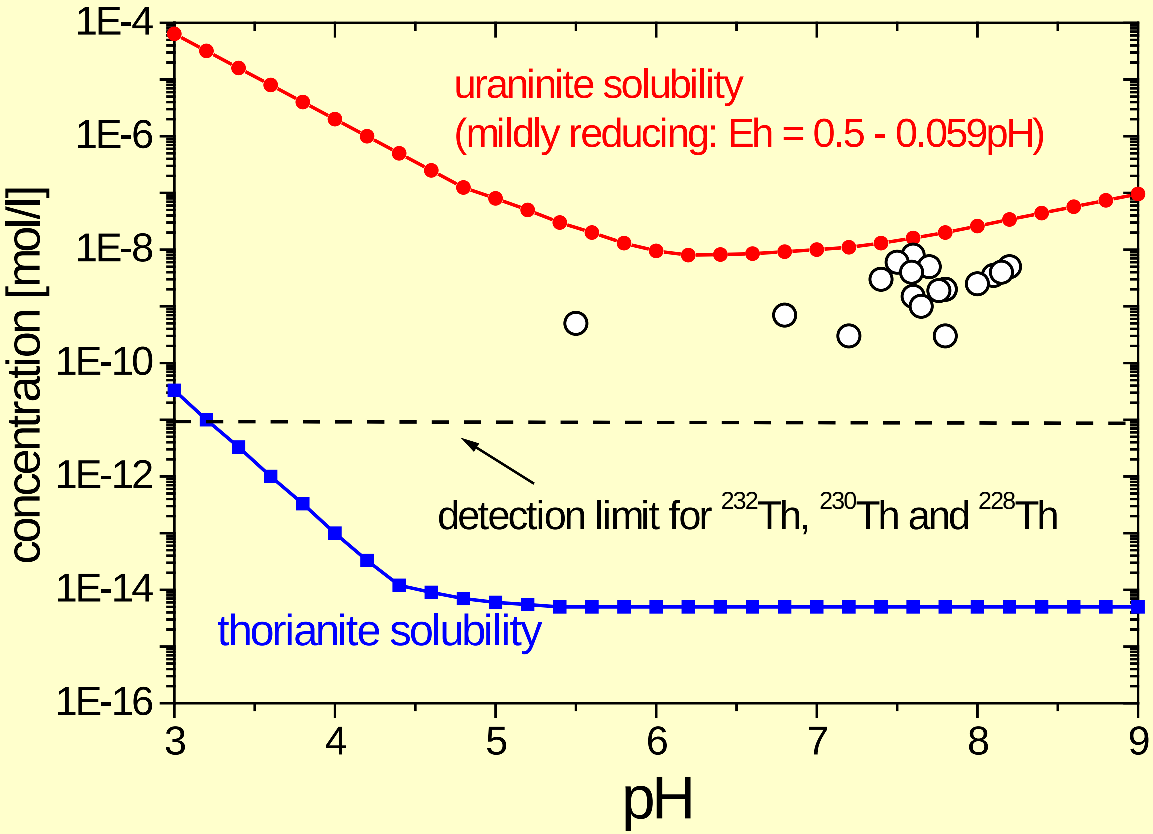
$$HCO_3^- \leftrightarrow CO_2 + OH^-$$

$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+$$

$$Ca^{2+} + CO_3^{2-} \leftrightarrow CaCO_3$$

$$2HCO_3^- + Ca^{2+} \leftrightarrow CaCO_3 \downarrow + CO_2 \uparrow + H_2O$$

Ingrowth of ^{230}Th without an inherited component, why that ?



^{226}Ra/^{230}Th/^{234}U dating principle

$$^{230}Th(t) = {}^{230}Th(0) \cdot e^{-\lambda\, 230t} + {}^{234}U \cdot (1 - e^{-\lambda\, 230t})$$

$$\frac{^{230}Th(t)}{^{232}Th} = \frac{^{230}Th(0)}{^{232}Th} \cdot e^{-\lambda 230t} + \frac{^{234}U}{^{232}Th} \cdot (1 - e^{-\lambda 230t})$$

$$^{234}U_{aut} = {}^{234}U_m - k \cdot {}^{232}Th_m$$

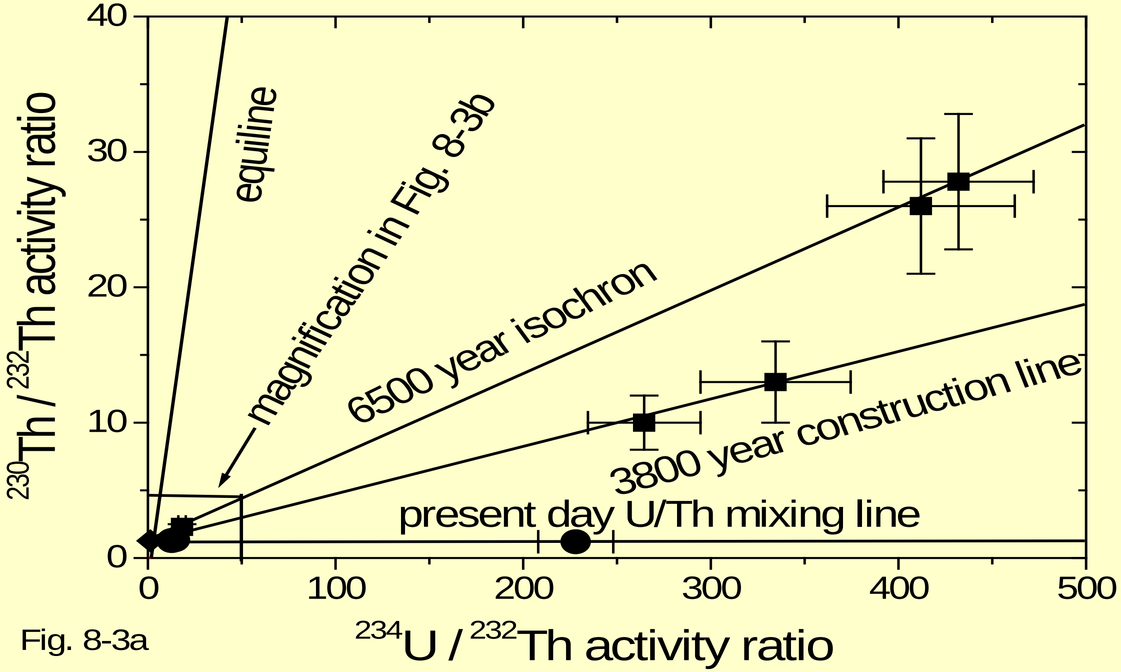


Fig. 8-3a

^{226}Ra/^{230}Th/^{234}U dating principle

$$^{230}Th(t) = {}^{230}Th(0) \cdot e^{-\lambda_{230} t} + {}^{234}U \cdot (1 - e^{-\lambda_{230} t})$$

$$\frac{^{230}Th(t)}{^{232}Th} = \frac{^{230}Th(0)}{^{232}Th} \cdot e^{-\lambda_{230} t} + \frac{^{234}U}{^{232}Th} \cdot (1 - e^{-\lambda_{230} t})$$

$$^{234}U_{aut} = {}^{234}U_m - k \cdot {}^{232}Th_m$$

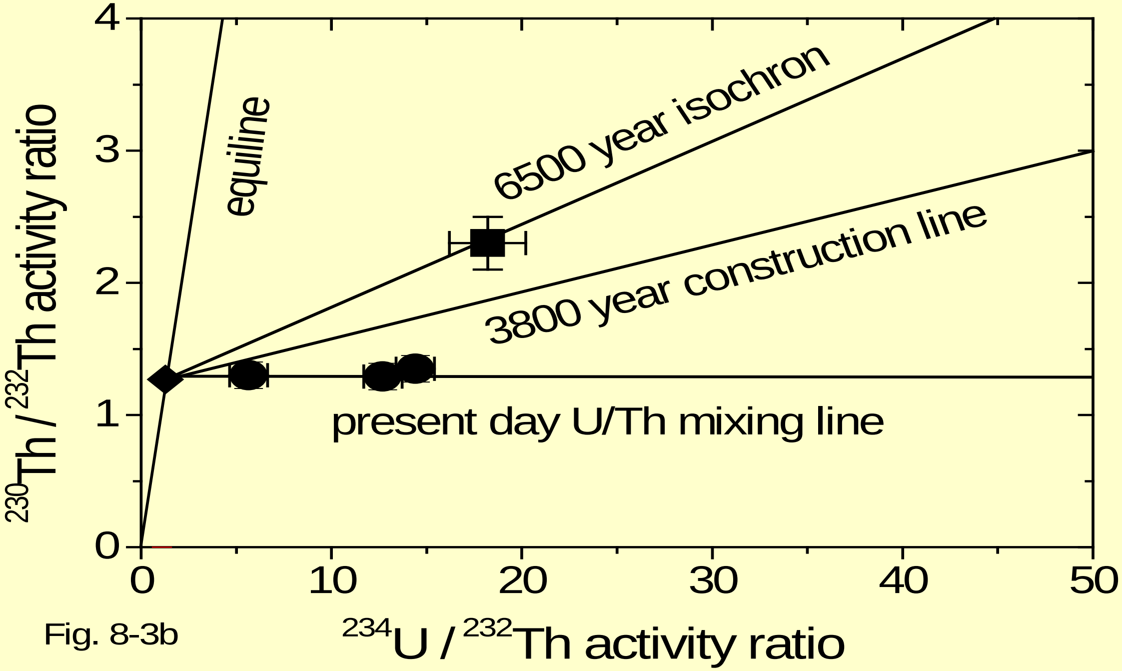
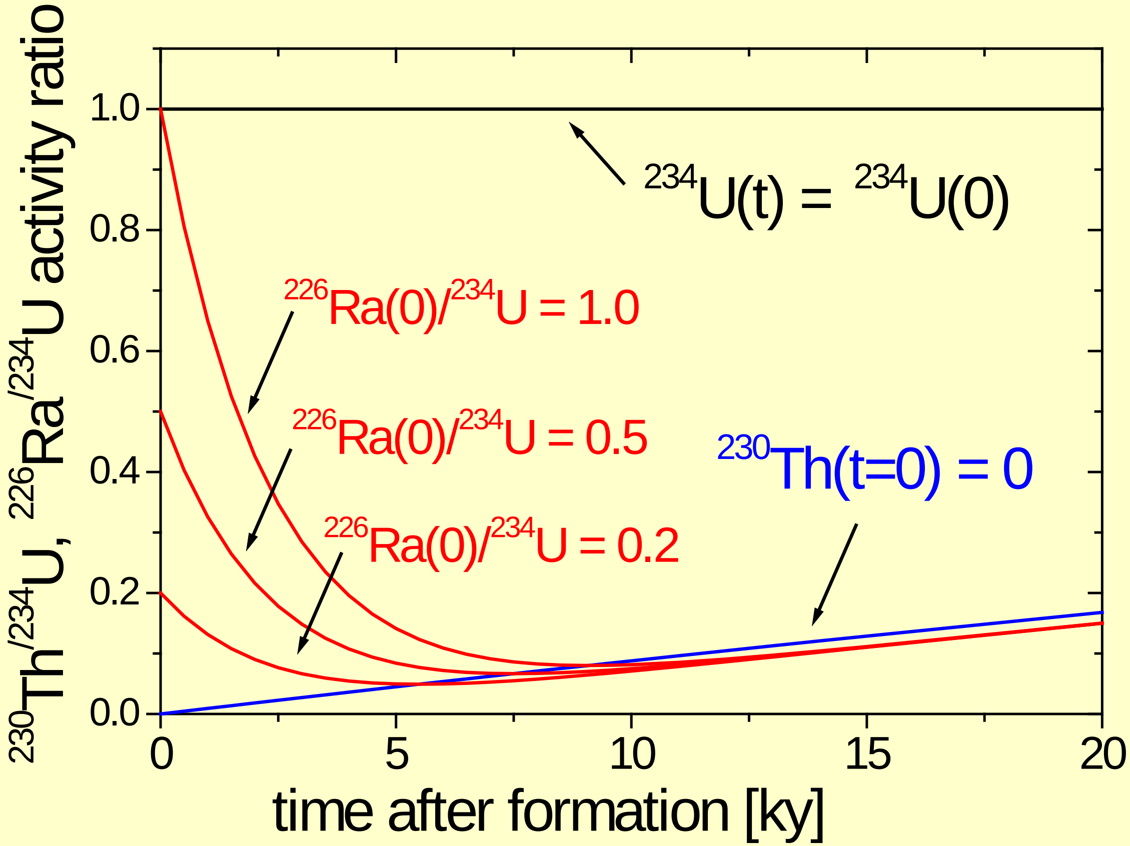


Fig. 8-3b

^{226}Ra/^{230}Th/^{234}U dating principle

$$^{230}Th(t) = {}^{230}Th(0) \cdot e^{-\lambda_{230} t} + {}^{234}U \cdot (1 - e^{-\lambda_{230} t})$$

Let's find an analytical (not numerical) solution for the propagation of the ^{226}Ra activity with time



^{226}Ra/^{230}Th/^{234}U dating principle

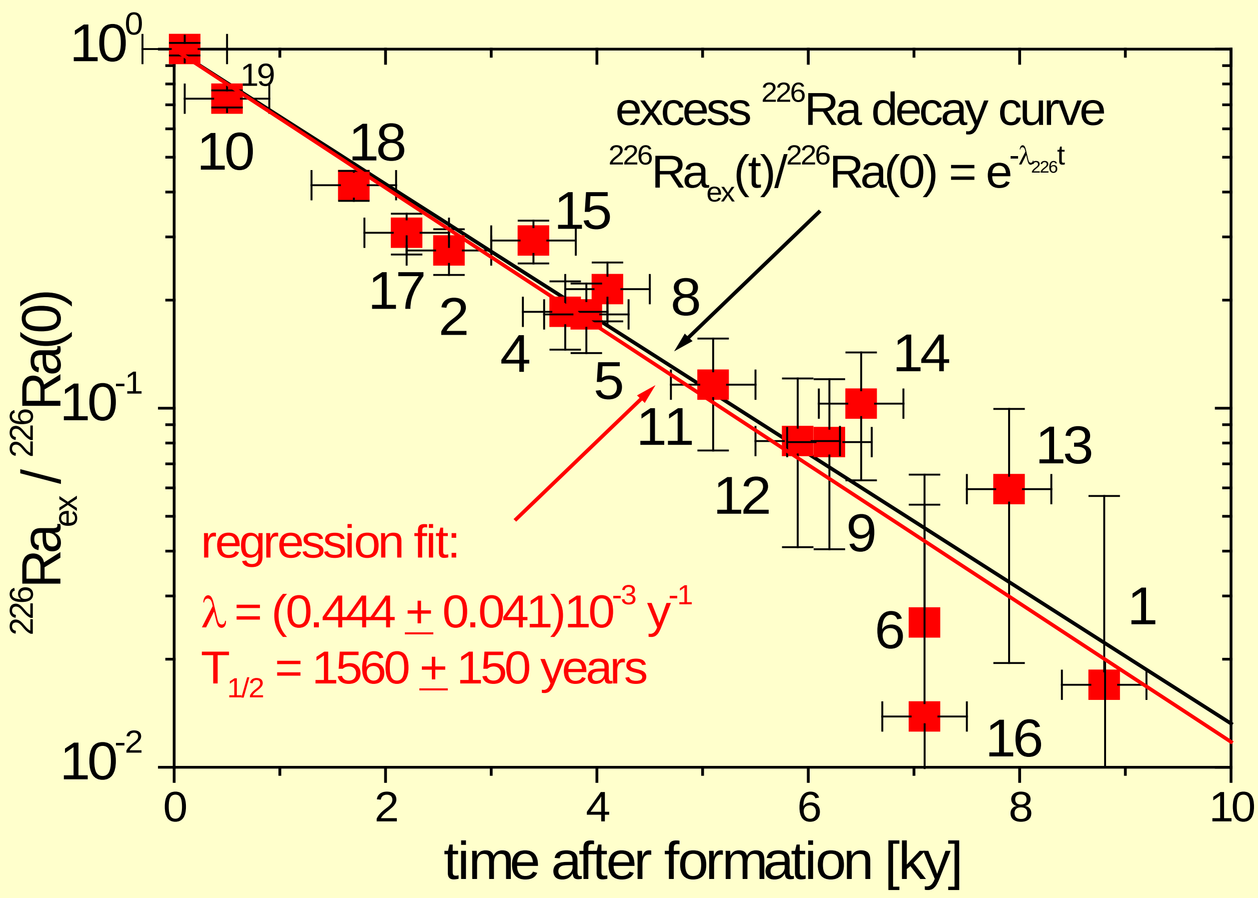
$$^{226}Ra(t) = {}^{226}Ra(0)\cdot e^{-\lambda_{226}t} + {}^{234}U \cdot \frac{\lambda_{226}\cdot(1-e^{-\lambda_{230}t}) - \lambda_{230}\cdot(1-e^{-\lambda_{226}t})}{\lambda_{226}-\lambda_{230}}$$

$$^{226}Ra_{ex}(t) = {}^{226}Ra_{aut} - {}^{226}Ra_{\sup}(t) \qquad {}^{226}Ra_{aut} = {}^{226}Ra_{m} - k\cdot{}^{232}Th_{m}$$

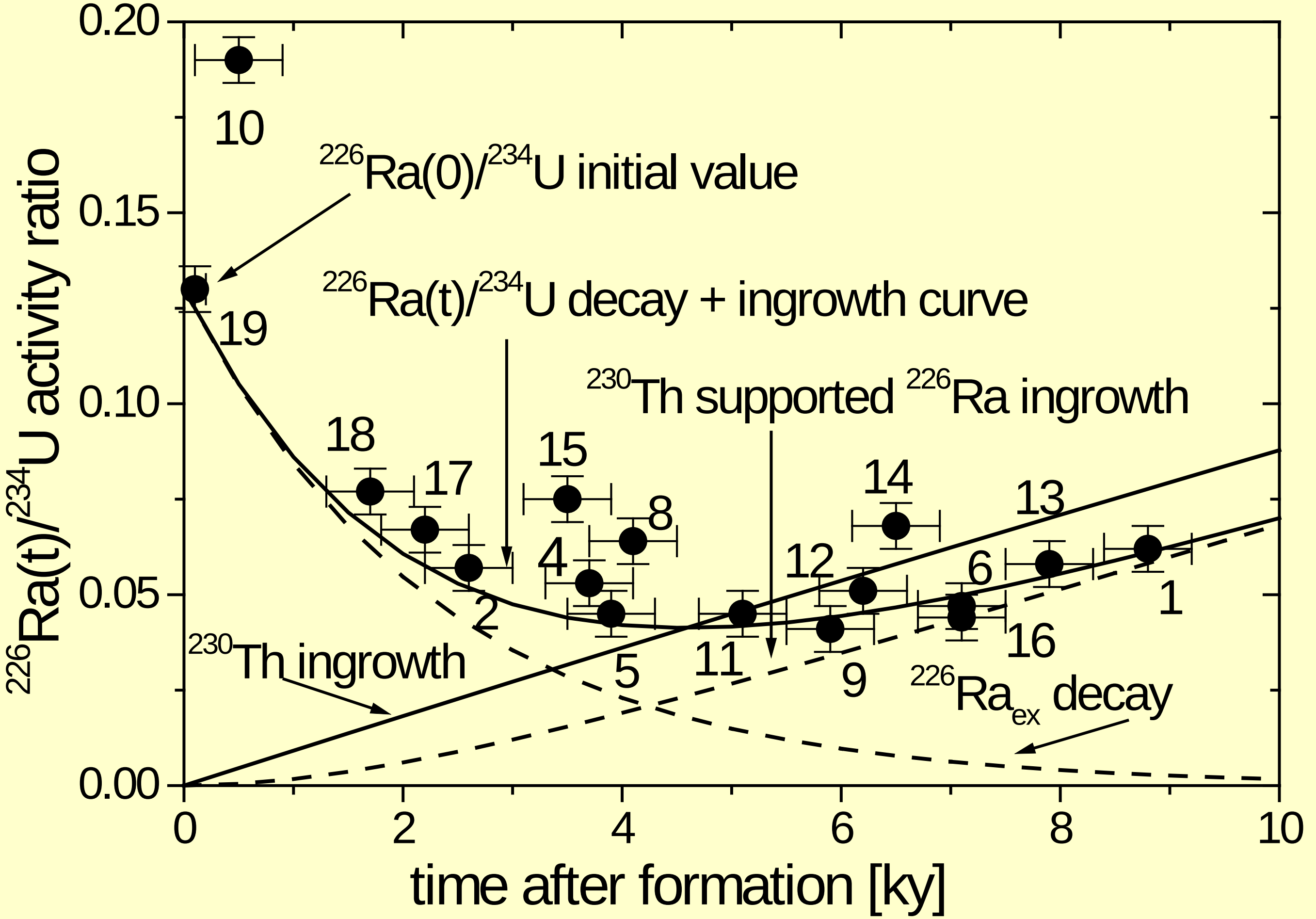
$$\frac{^{226}Ra_{ex}(t)}{^{226}Ra(0)} = \frac{^{226}Ra_{aut} - {}^{226}Ra_{\sup}(t)}{^{226}Ra(0)} = e^{-\lambda_{226}t} \qquad t_{age} = -\frac{1}{\lambda_{226}}\cdot\ln\left(\frac{^{226}Ra_{aut} - {}^{226}Ra_{\sup}(t)}{^{226}Ra(0)}\right)$$

$$F(t) = \frac{^{226}Ra_{aut} - {}^{226}Ra_{\sup}(t)}{^{226}Ra(0)} - e^{-\lambda_{226}t}$$

Validating the model with the sample data



Calculating $^{226}Ra_{ex}$-ages analytically with the assumption of constant $Ra_{ex}/^{234}U$ ratios



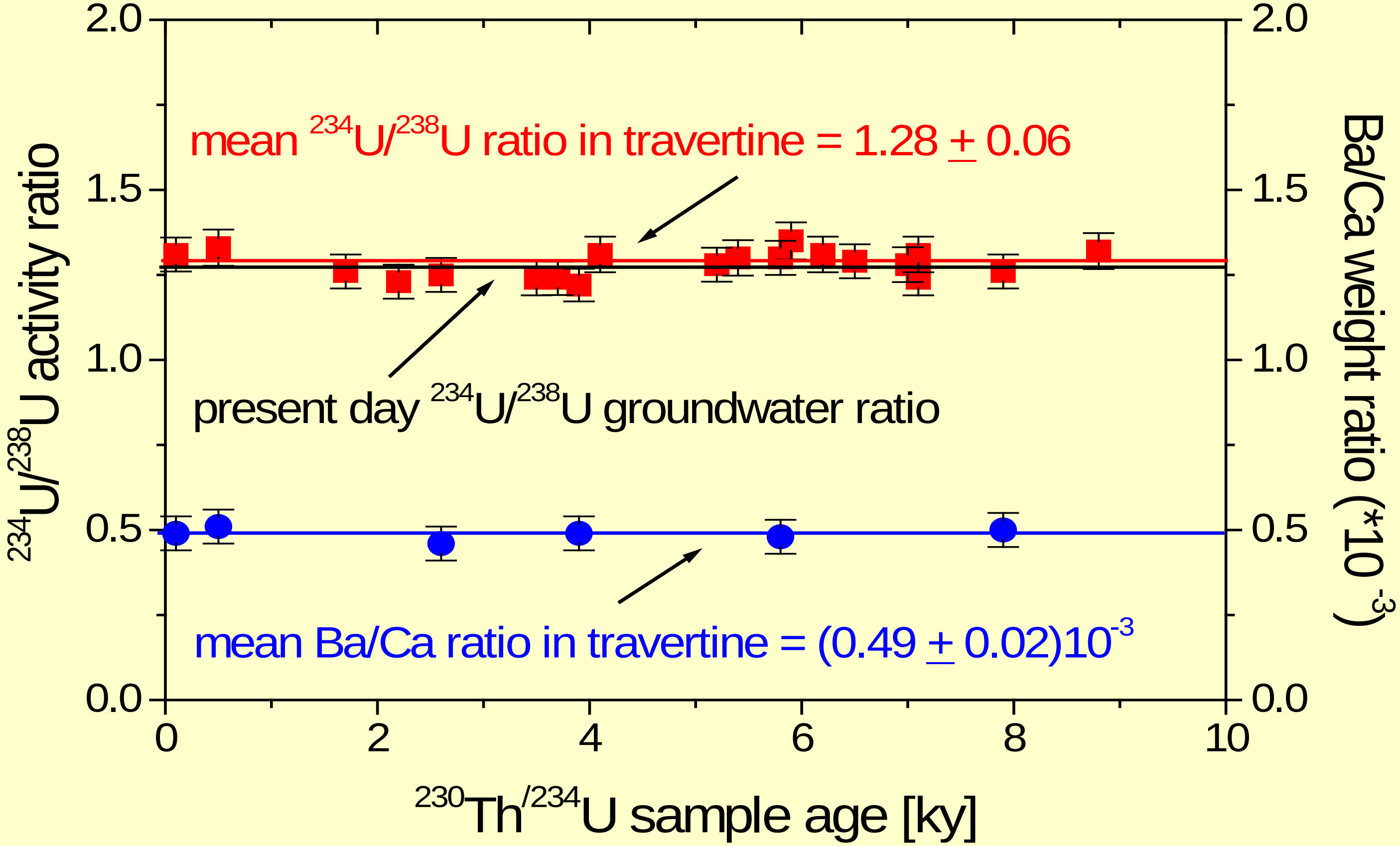
Periodic Table of the Elements

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	↑	Rf	Db	Sg	Bh	Hs	Mt	...	...	...						

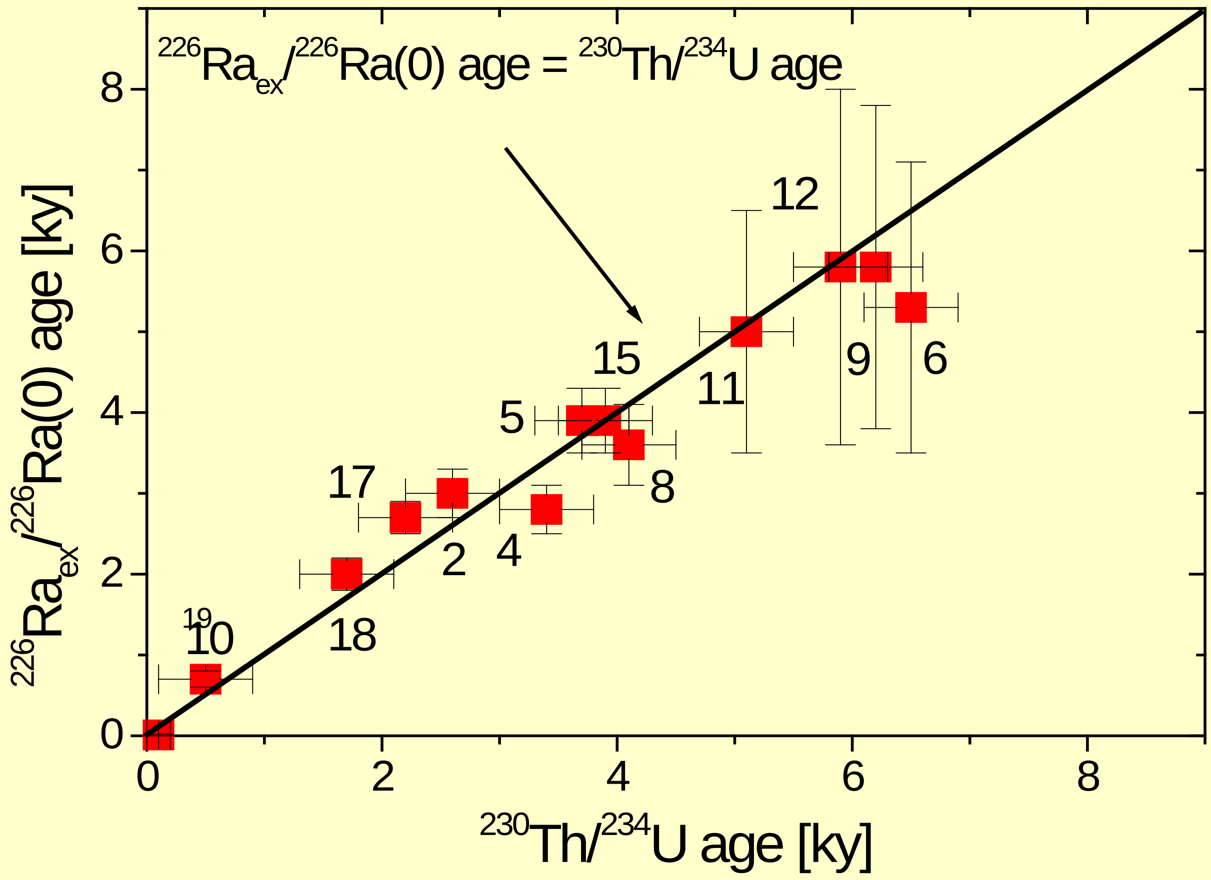
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

- alkali elements
- group 3a-6a elements
- transition elements
- halogens
- lanthanides and actinides
- noble gases

Reasons for a stable aqueous chemistry, i.e. constant initial $^{226}Ra(0)$

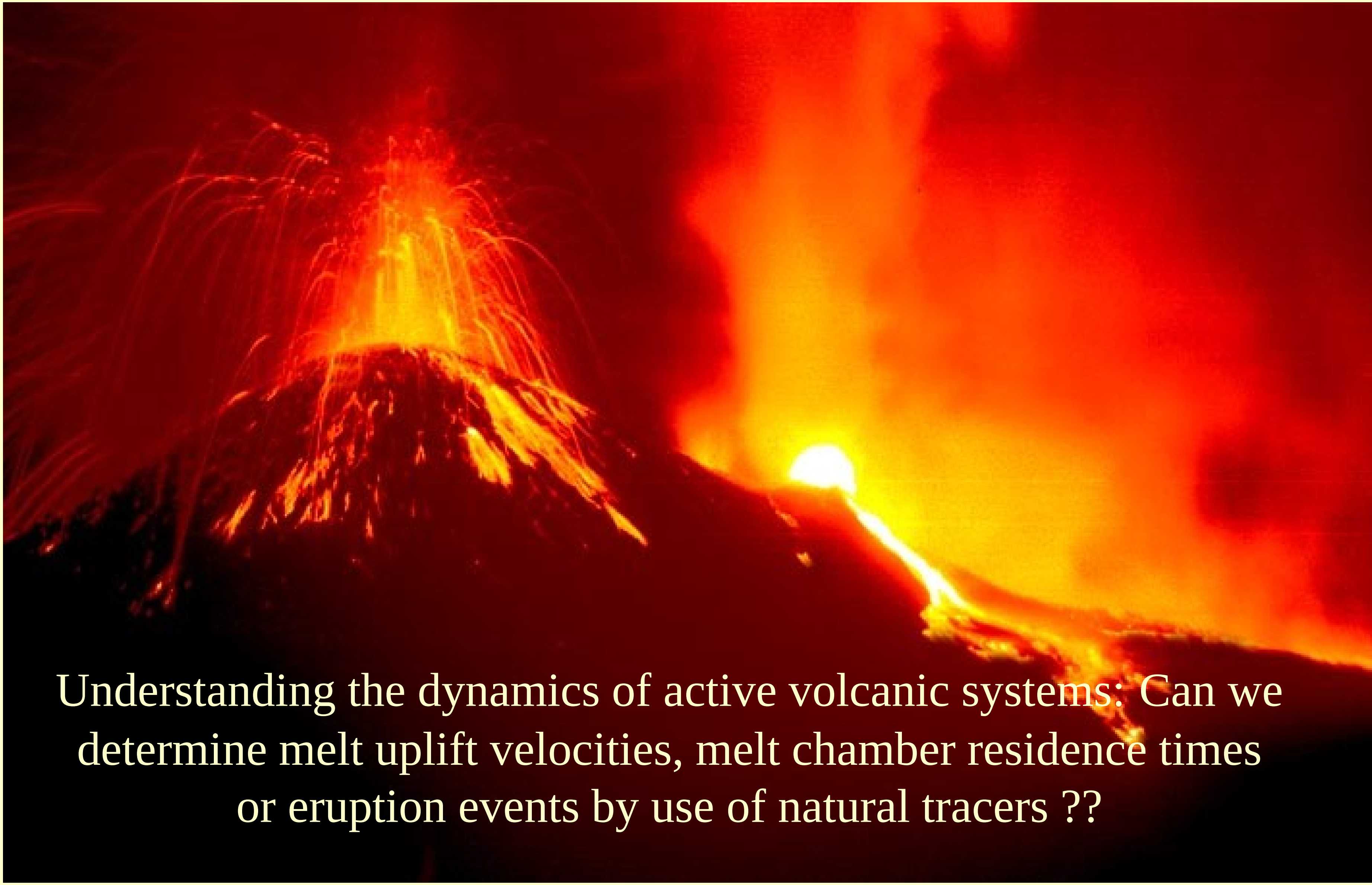


Comparing $^{226}Ra_{ex}$/ $^{226}Ra(0)$ with $^{230}Th/^{234}U$ ages

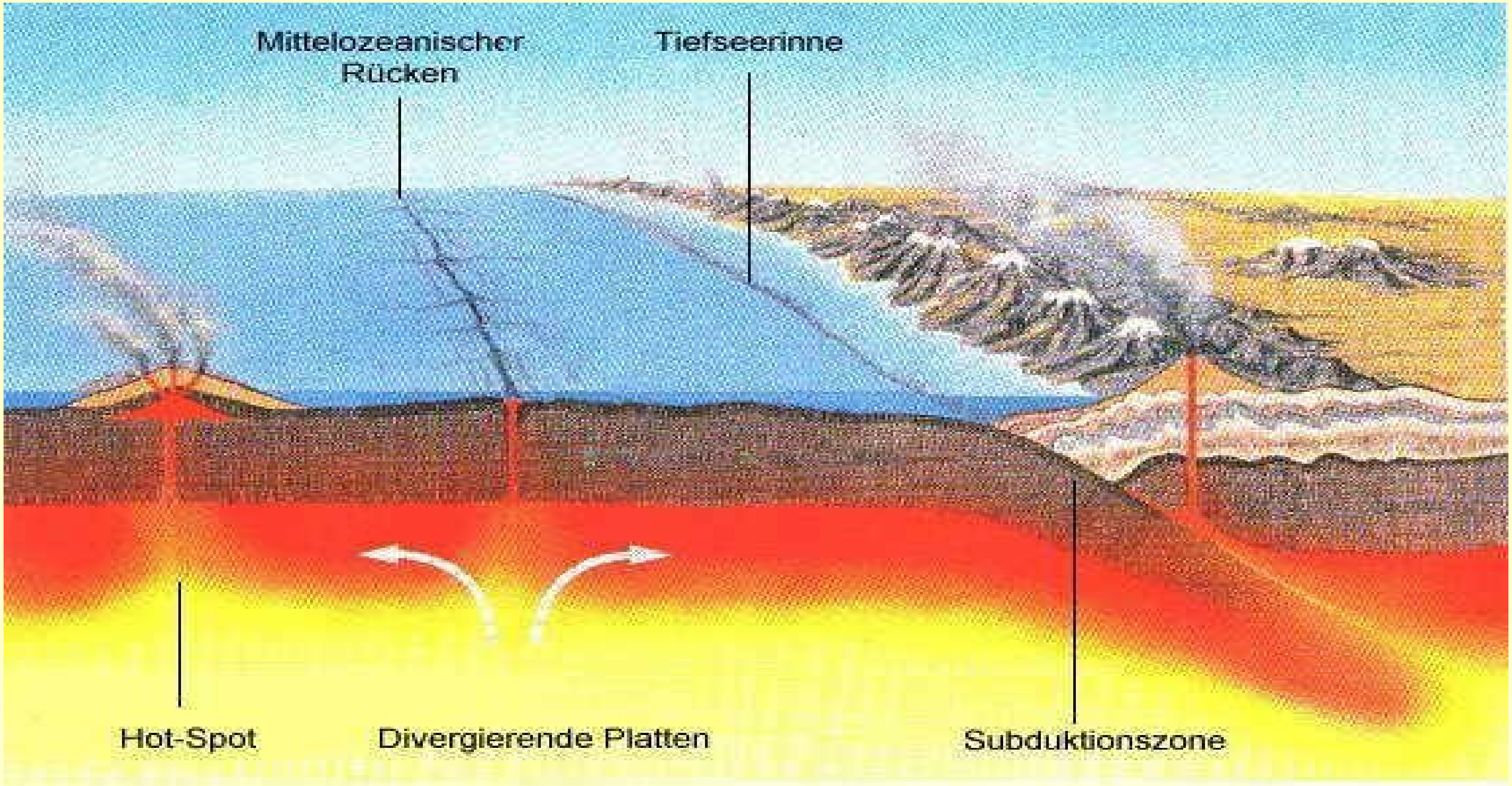


Conclusions

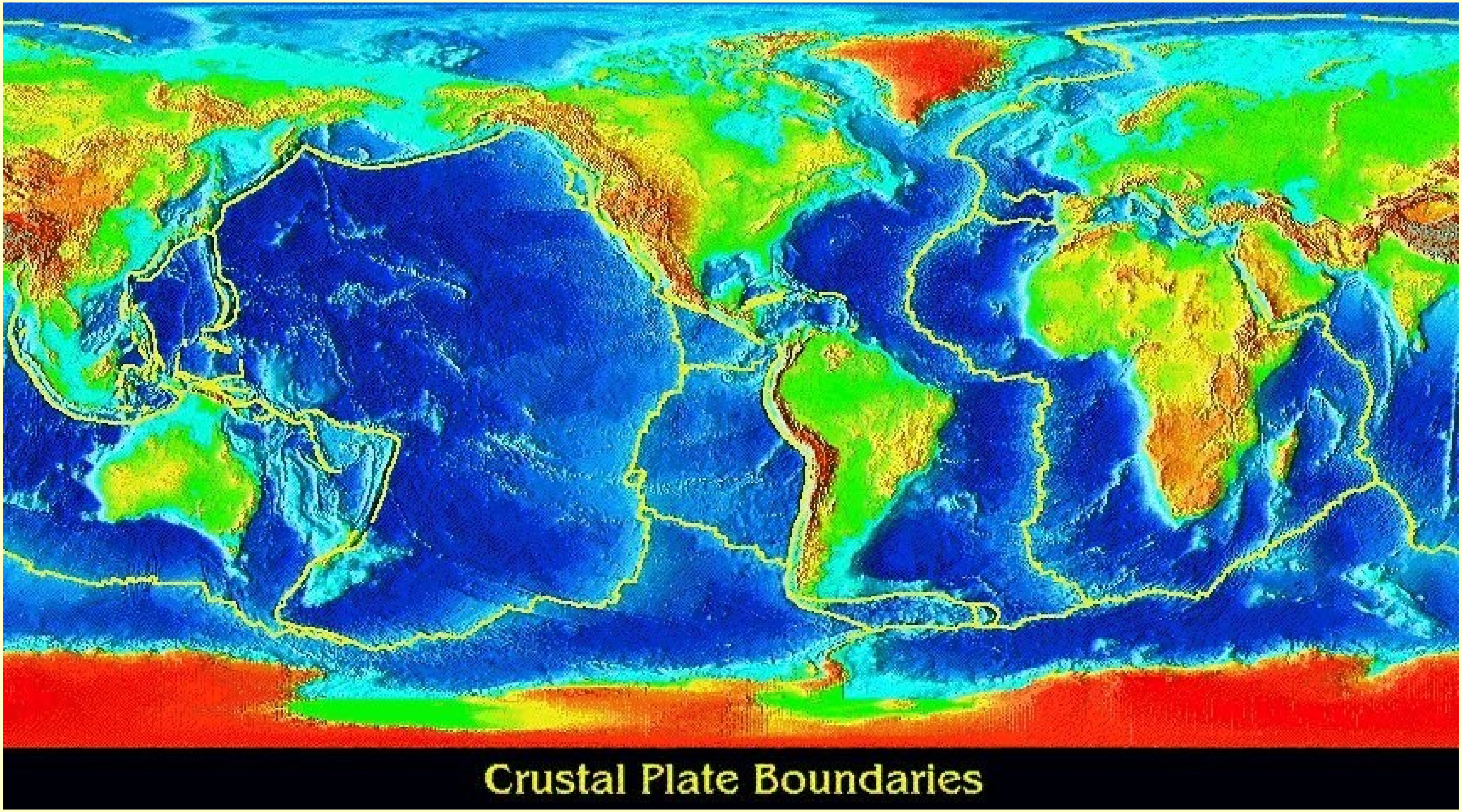
- $^{230}Th/^{234}U$ and $^{226}Ra_{ex}/^{234}U$ two chronometer dating yields consistent results (agreeing ages)
- Inherited ^{230}Th at sample formation is negligible
- The chemical groundwater composition seems to be highly uniform, obviously there is almost no change of the ^{226}Ra-initial with time


Understanding the dynamics of active volcanic systems: Can we determine melt uplift velocities, melt chamber residence times or eruption events by use of natural tracers ??

The dynamic earth: sea floor spreading and subduction of oceanic plates



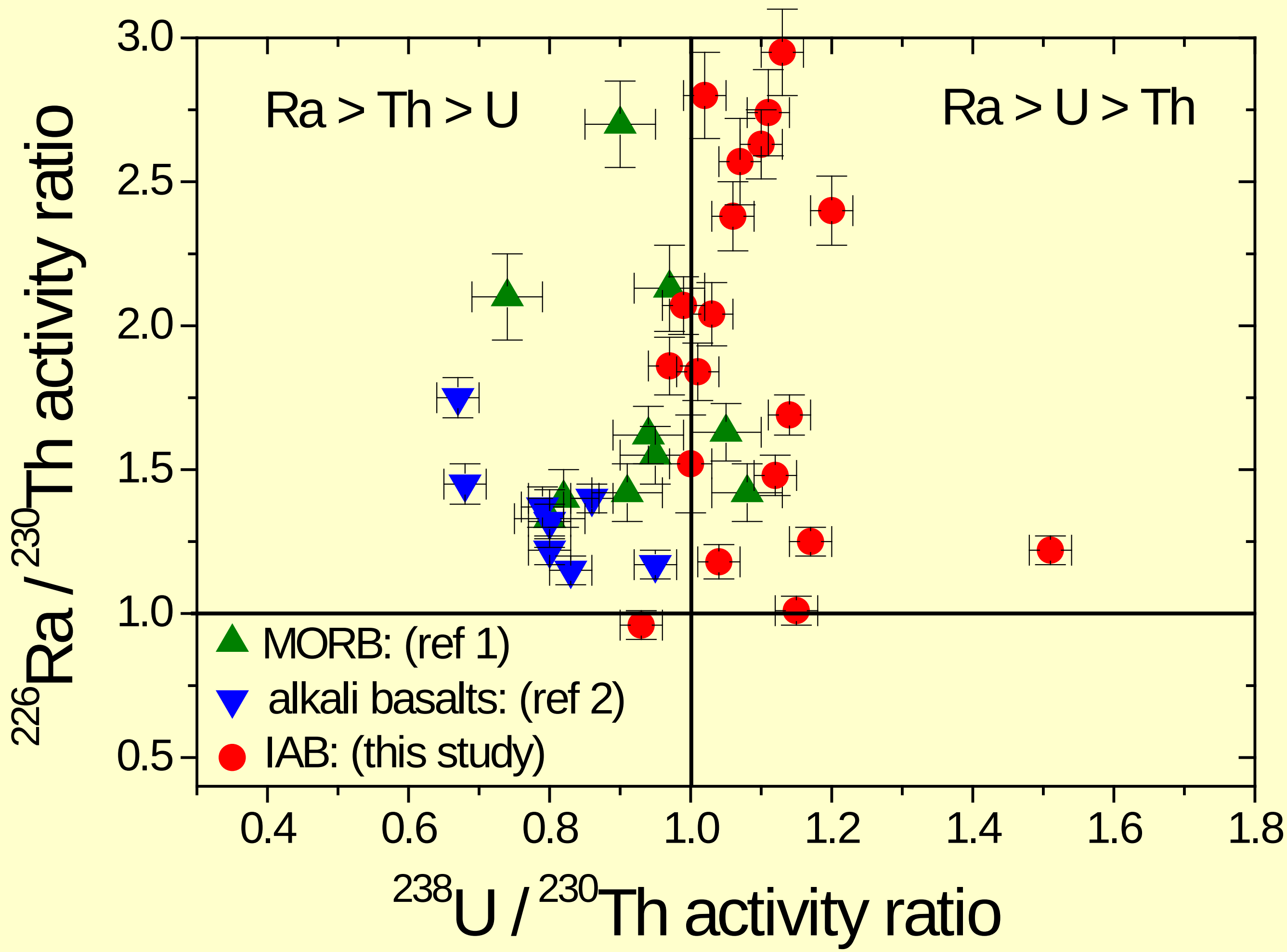
Study objects: island arc volcanic rocks from the Sunda-Banda subduction zone



Which radio-tracers can be applied ?

Isotope	Half-life [years]	Suitable time span
^{230}Th	76000	2000 – 200000
^{231}Pa	33000	1000 - 100000
^{226}Ra	1600	100 - 6000
^{210}Pb	22	3 - 100

U-Th-Ra fractionation during melt differentiation




Thank you for your attention