7. Age determination

7.1 Historical back ground

7.2 Relative age determinations

7.3 Absolute age determinations

7.3.1 Geochemical-physical background

7.3.2 Analytics

7.3.3 Selected methods for age determination

7.3.3.1 Cosmogenic nuclides (e.g. ^{14}C)

7.3.3.2 K/Ar and Ar/Ar methods

7.3.3.3 Rb-Sr and Sm-Nd isochron methods

7.3.3.4 U methods

7.3.3.5 Fission track method

7.3.3.6 Luminiscense method

7.3.3.7 Determination of the cooling history of rock

7.1 Historical background

- ➔ Stratigraphical principle of Nils Steno ➔more than 200 epochs of the earths history are characterised by fossils which document characteristic climatic and environmental conditions
- ➔ Radiogenic isotopes and development of mass spectrometers between AD 1940 to 1950
  ➔Absolute ages of rocks

Physical pioneers of age deteremination methods

- 1895 Dicovery of X-rays by C. Röntgen
- 1896 Discovery of radition from the element Uranium by H. Becquerel
- 1898 Discovery of the radioactivity by Marie Curie

⇨ Milestones with respect to age determinations which was the basis for a better understanding of the evolution of our planetary system and the evolution of the earth

- The basic concept for radiometric age determination by E. Rutherford
- Development of various age deteremionation methods based on improvde knowledege of radioactive decays of elements, e.g. the ^{14}C-method in 1947 .

7.2 Relative age determinations

➔characteristic age related pattern of sediment records:

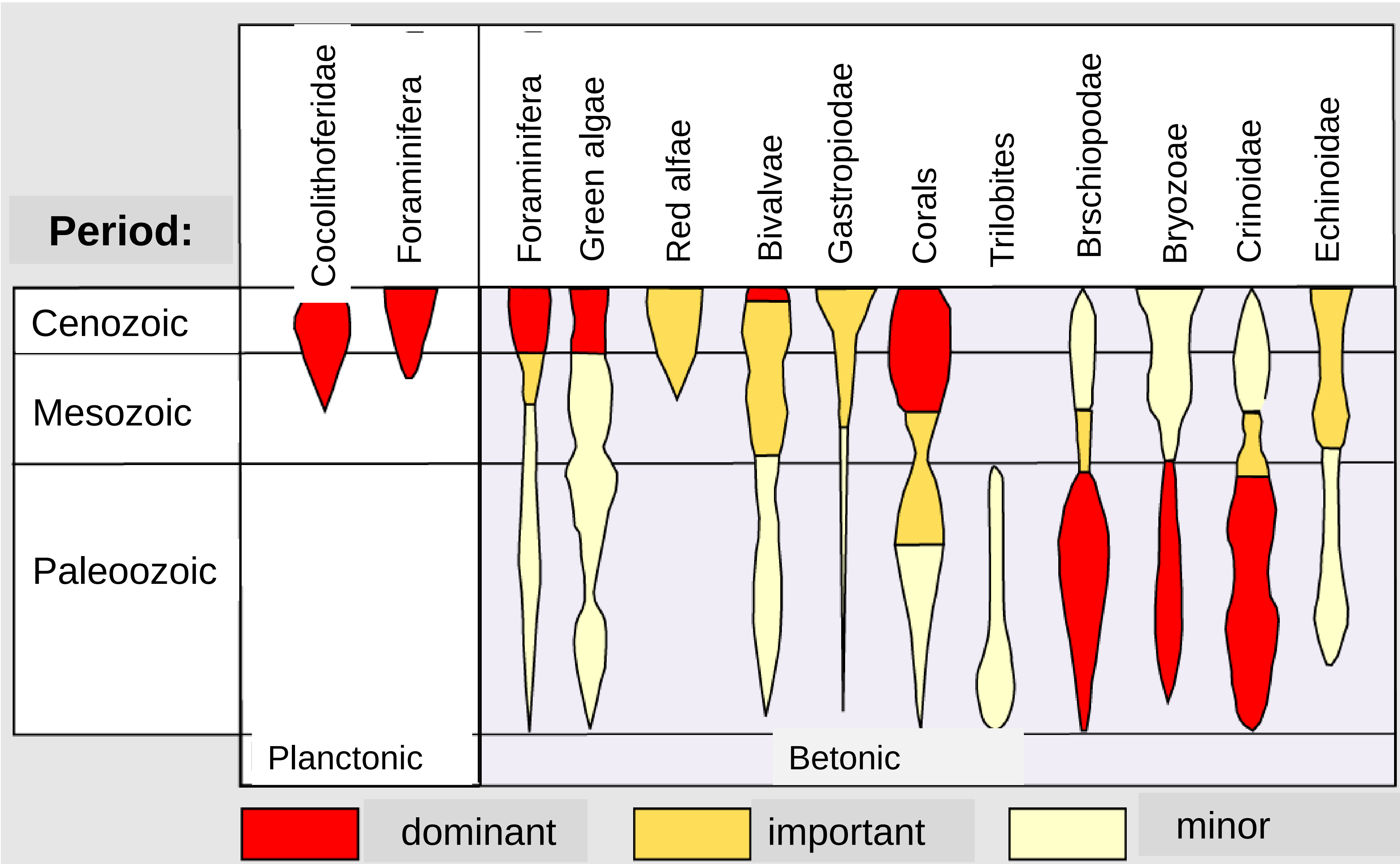
Paleomagnetism: ferromagnetic properties of minerals in volcanic or sedimentary rocks ➔Orientation of the earths magnetic field is „frozen“ and can indicate a relative or partly absolute time scale

Pattern of oxygene isotopes in ice core or biogenic carbonates of sediment records

Pattern of pollen: Glacial-interglacial cycles of the Quaternary produced typical pattern

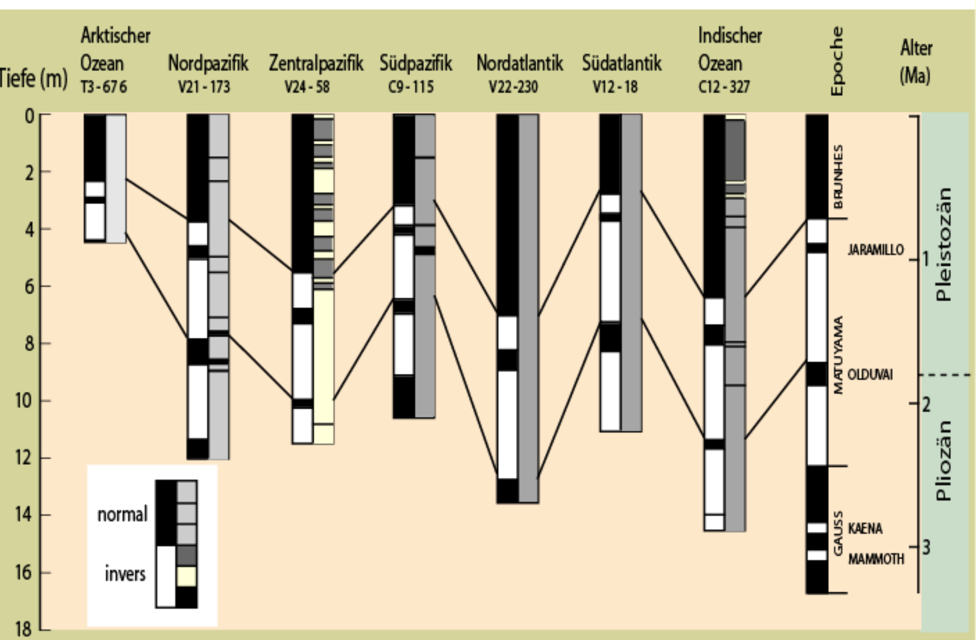
Index fossils: which incate animals which were living only short periods, but had a large regional distribution

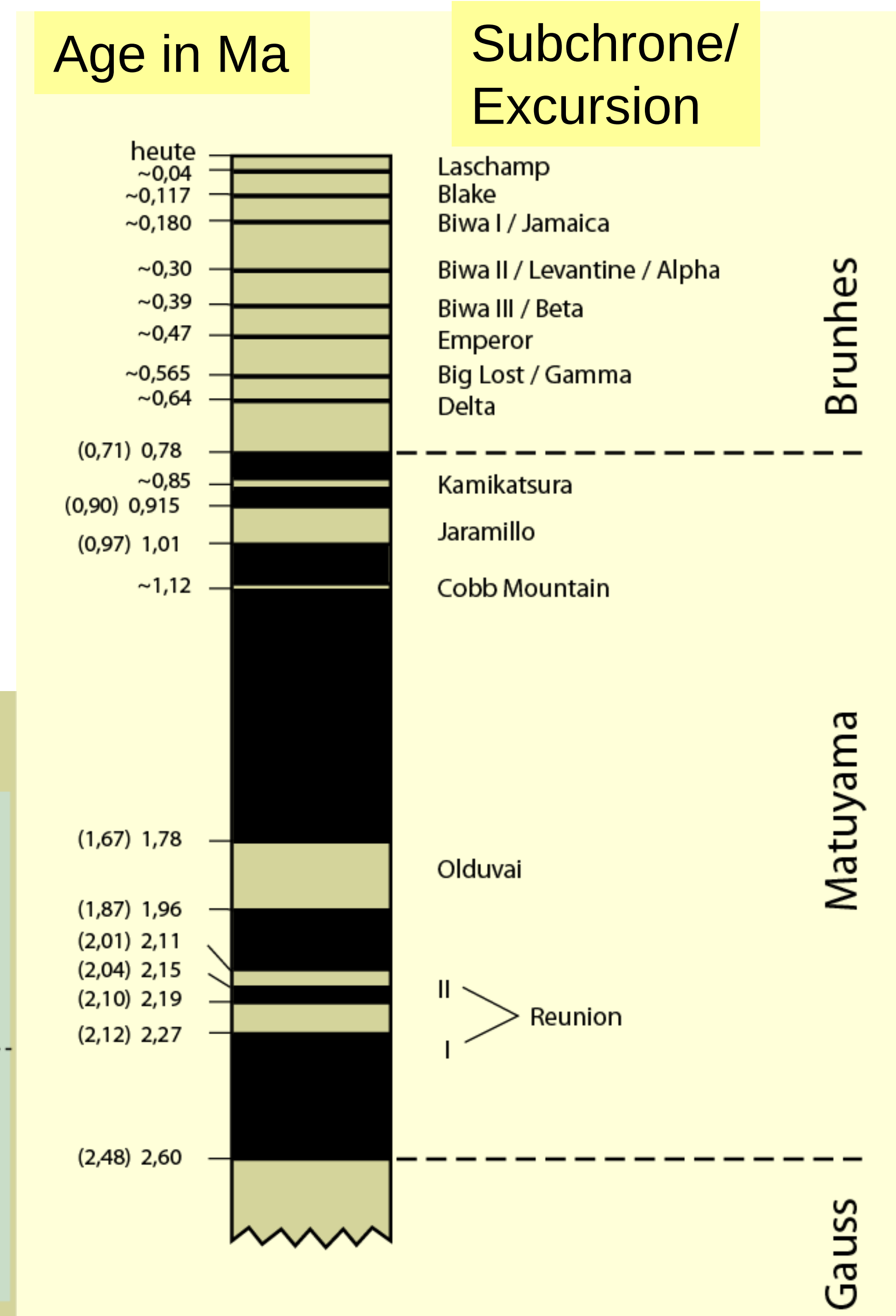
Index fossils are termend paleontological remnants of animals which lived during a short period in the earths history, but had a large regional distribution.



Wilkinson (1979)

Magnetic anomalies can be used for a relative and absolute age determination, if the timing of pole reversals have been dated by absolute radiogenic age determination of magmatic rocks (Figure right). Sediment cores can be synchronisized (see below).

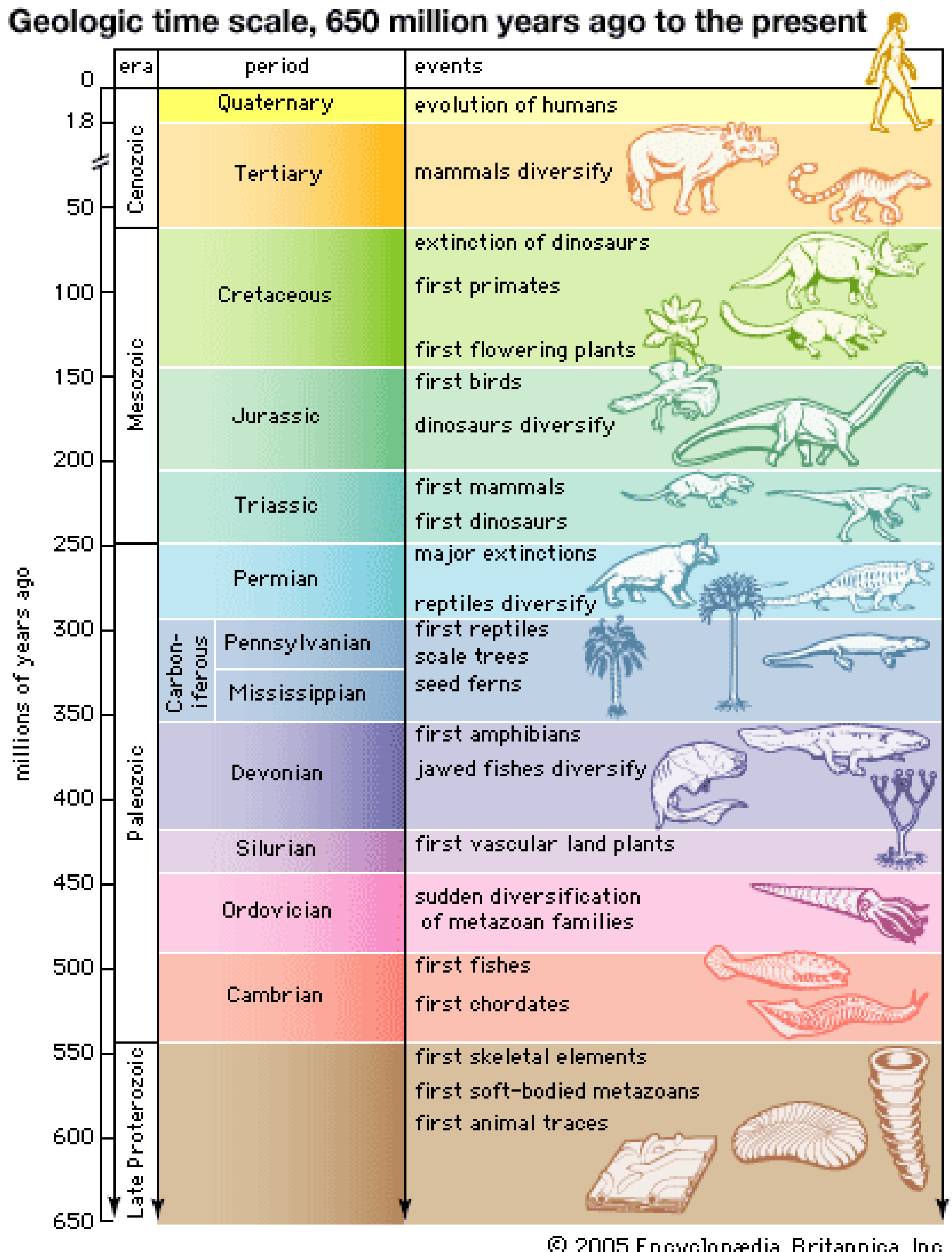




Geomagnetische Polaritätsskala (aus Wagner 1995, wo zahlreiche Primärreferenzen gegeben sind)

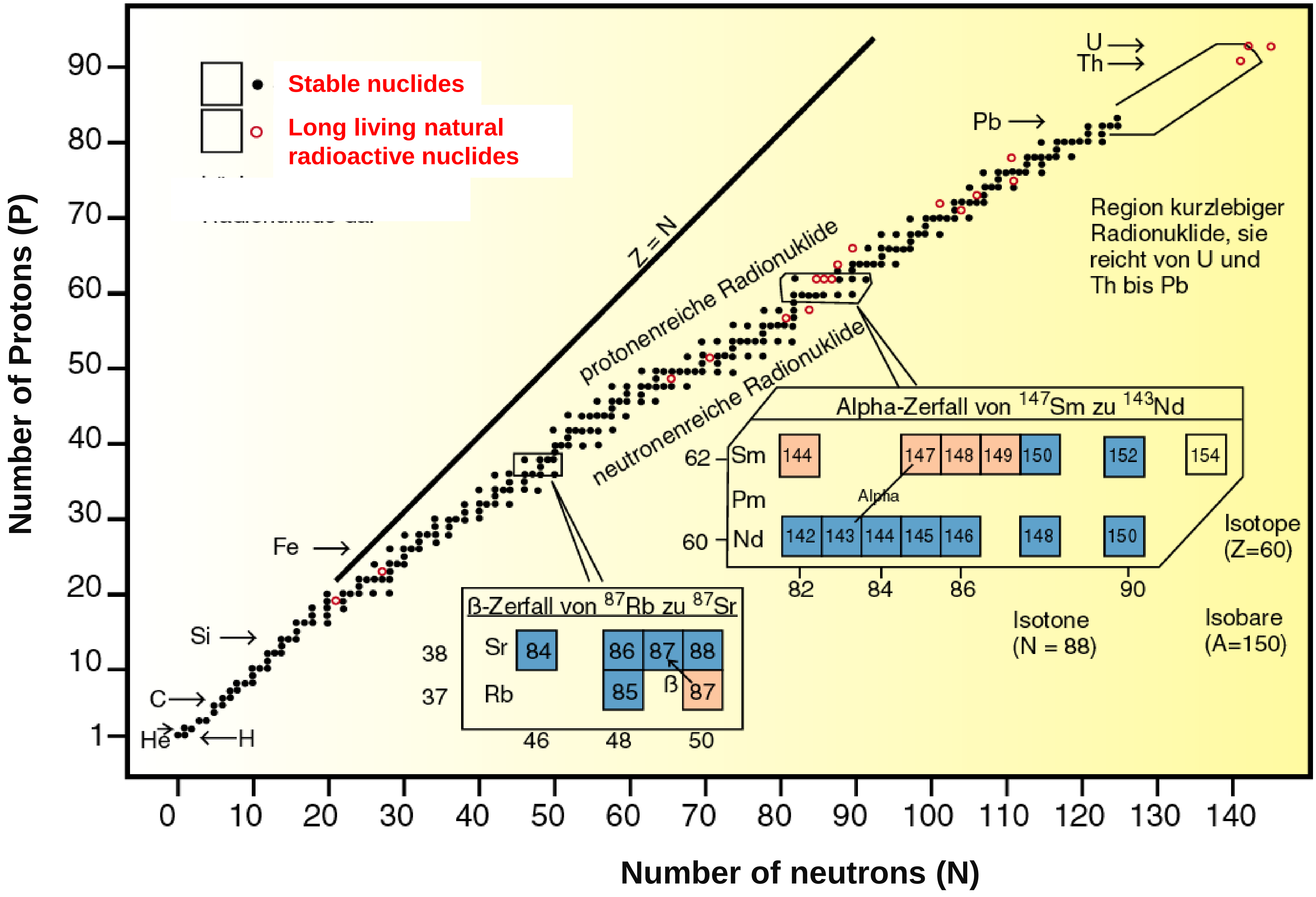
7.3 Absolute age determination

Geological time scale.

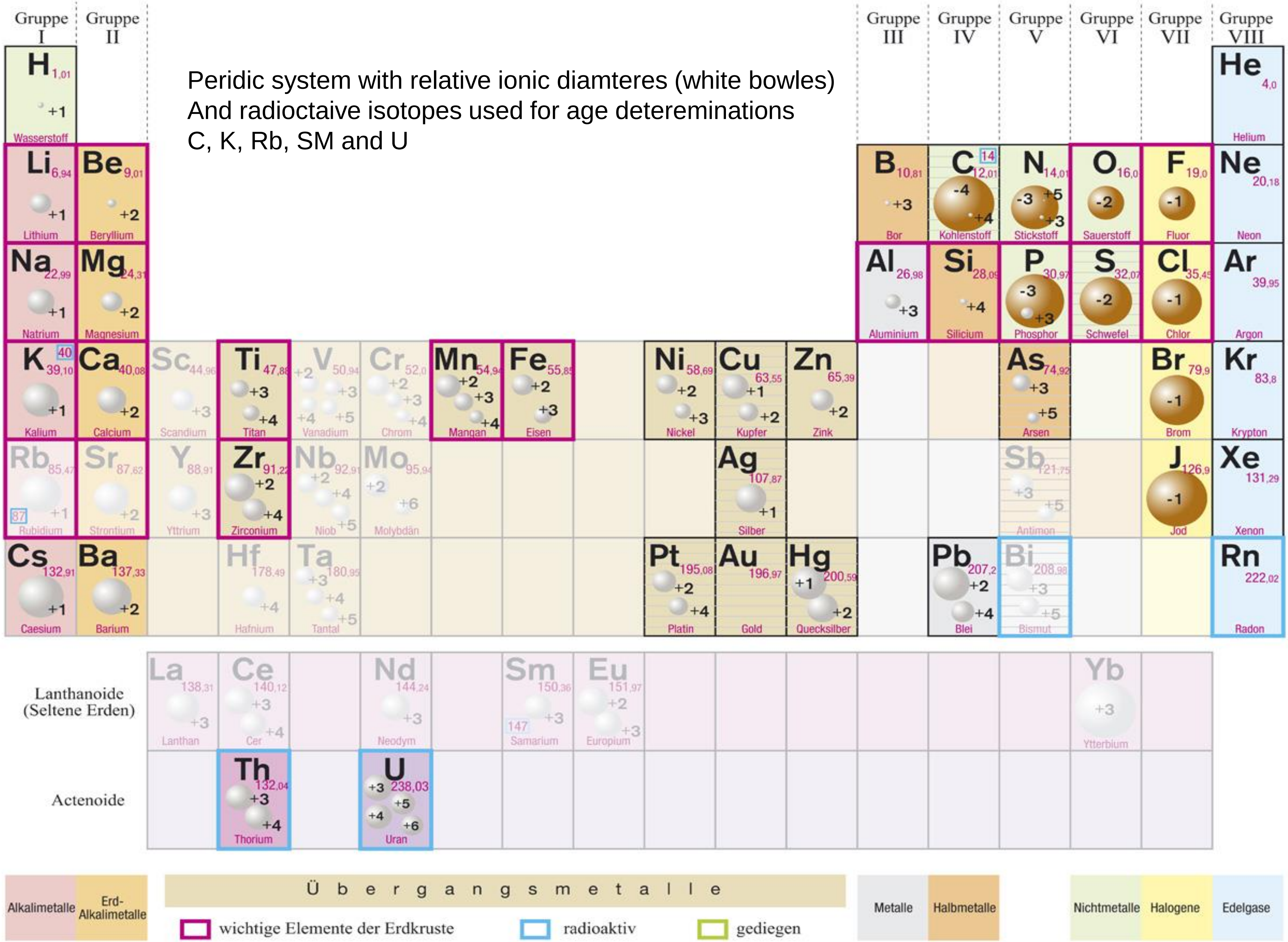


http://www.rcom.marum.de/Binaries/Binary15353/Erdzeitalter.jpgArial

7.3.1 Geochemical and physikalic back ground: Each element is characterised by a certain number of protons, but it can appear with different numbers of neutrons in the nucleus which are called isotopes. Radiogenc nuclides are marked in red circles.



Peridic system with relative ionic diamteres (white bowles)
And radioctaive isotopes used for age deteremінations
C, K, Rb, SM and U



Periodensystem modifiziert nach K. Becker

What is radioactivity?

- One element includes different isotopes with different numbers of neutrons in the nucleus which each define a isotope with a number which indicates the total sum of protons and neutrons.

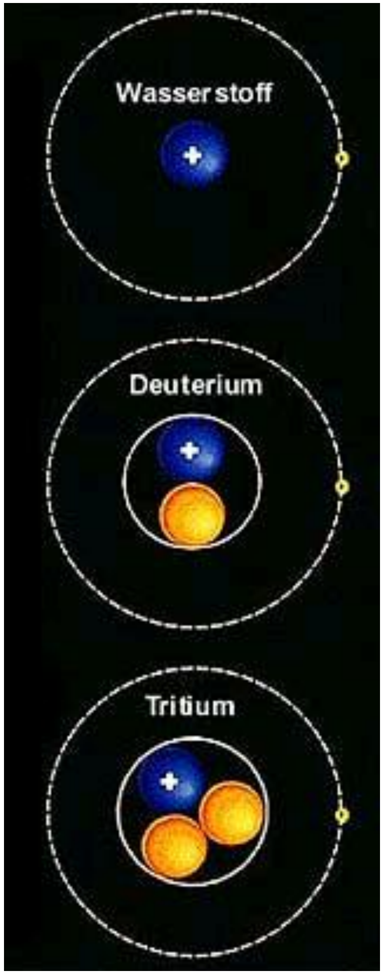
- Isotopes are nuclides with a defined number of nucleons (protonens and neutrons). Instable nuclidee are radioactive.

  e.g. ^{1}H (1 proton = 1 nucleon)

  ^{2}H bzw. D (1 proton + 1 neutron = 2 Nucleons)

  ^{3}H bzw. T (1 proton + 2 neutrons = 3 Nucleons)

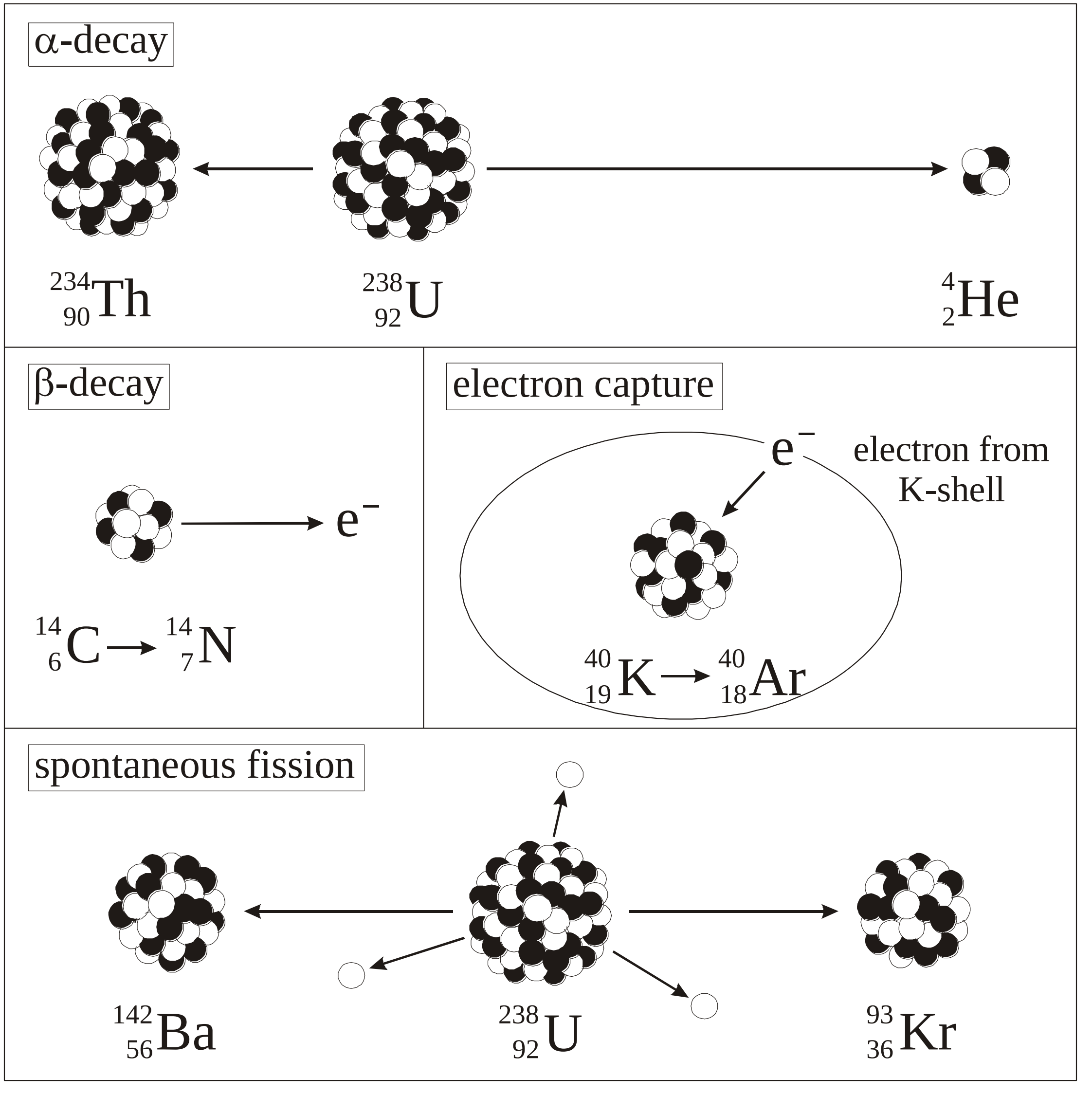
Proportion ^{1}H = 99,985 %, ^{2}H = 0,0145 %, ^{3}H = 10^{-16} %



Some radioactive nuclides and their half-life times:

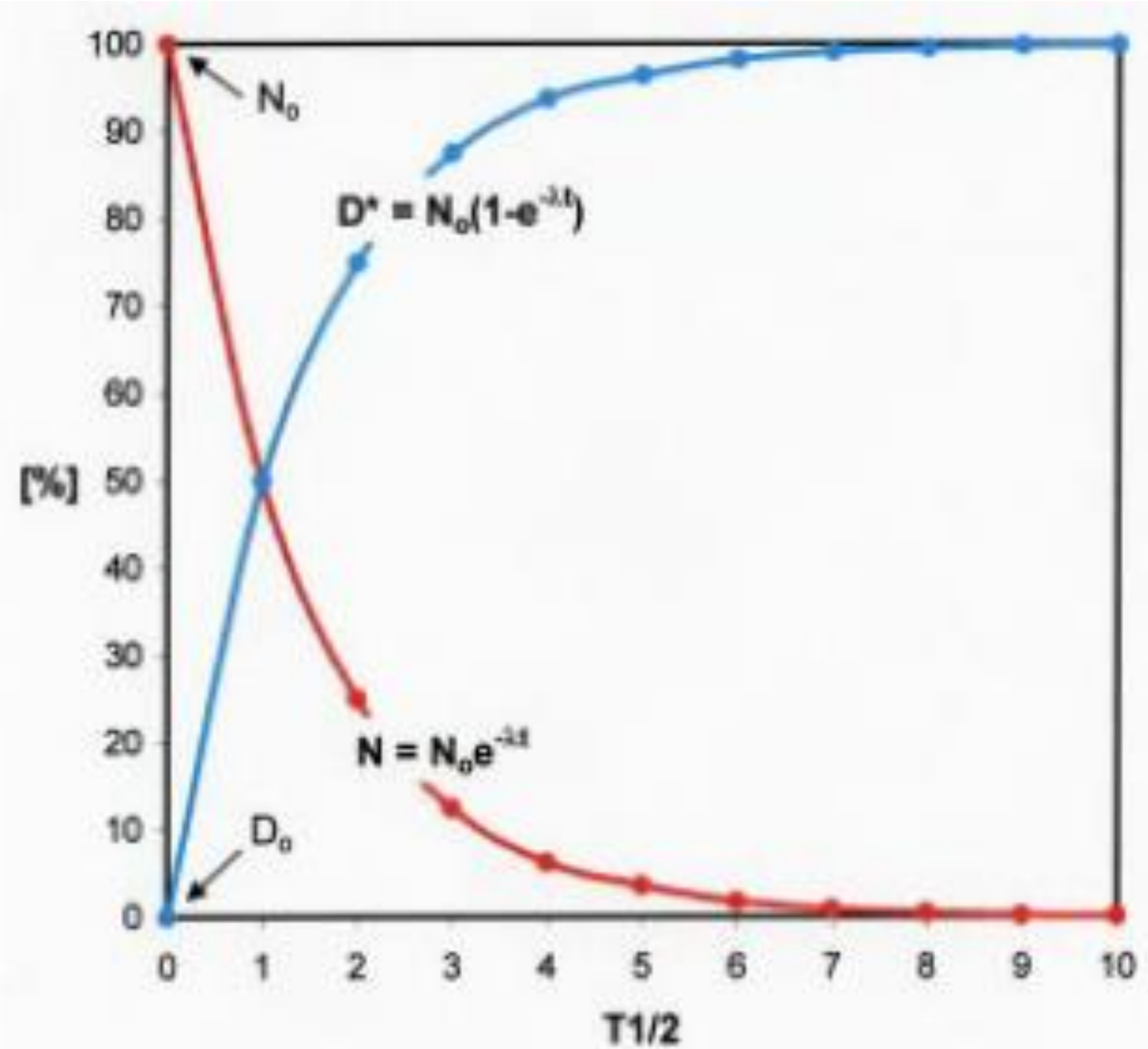
Nuclide	Half-live time (a)
^{10}Be	$1.5 \cdot 10^{6}$
^{14}C	5730 ± 40
^{40}K	$1.250 \cdot 10^{9}$
^{176}Lu	$3.3 \cdot 10^{10}$
^{87}Rb	$4.88 \cdot 10^{10}$
^{147}Sm	$1.06 \cdot 10^{11}$
^{235}U	$0.7038 \cdot 10^{9}$
^{238}U	$4.468 \cdot 10^{9}$

Example of different radioactive decays of the elements Th, C, K and Ba.



The radioactive decay causes an exponential de-crease of mother isotopes (N) and increase of the daughter isotopes (D).

Note that after 6 to 7 fold of the half-live time (T1/2) nearly all mother isotopes are decomposed.



Assumptions for the aplicability of age determination methods on geological samples

1. Closed system
2. Complete reset of the „age clock“ due to a geological event, which should be dated
3. Constancy of the individuel decay rates l:

(a) *for direct activity meassurements* : very high

(b) *for age determinations based on mother/daugther isotope relationships it should be*:

high enougth to obtain a sufficient high increase of daughter isotopes during the earths history

low enough to genug, to measure still a considerable amount of mother isotopes

4. Posibility to determine D_0

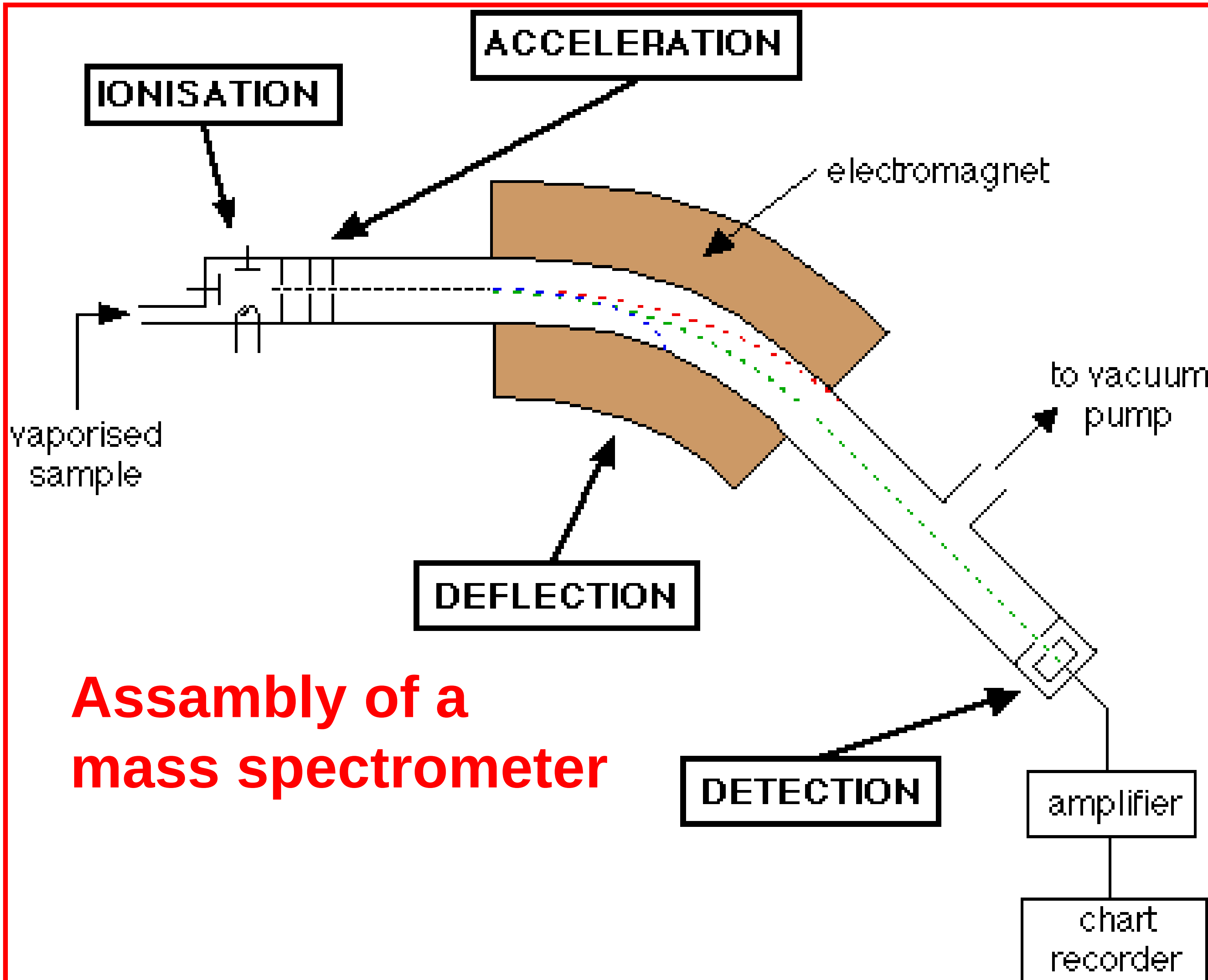
7.3.2 Analytics: Sample preparation

- ***Mechanical preparation and selection:***
  Crashing sieving, shaking, magnetic separation, separation based on different densities of minerals

- ***Chemical preparation for thermal ionistation mass spectrometrie:***
  Acid digestion of the minerals; separation of ions by chromatographical methods

- ***Chemical preparation for Gass mass spectrometers:***
  Cleaning and filtering of gases released from the minerals

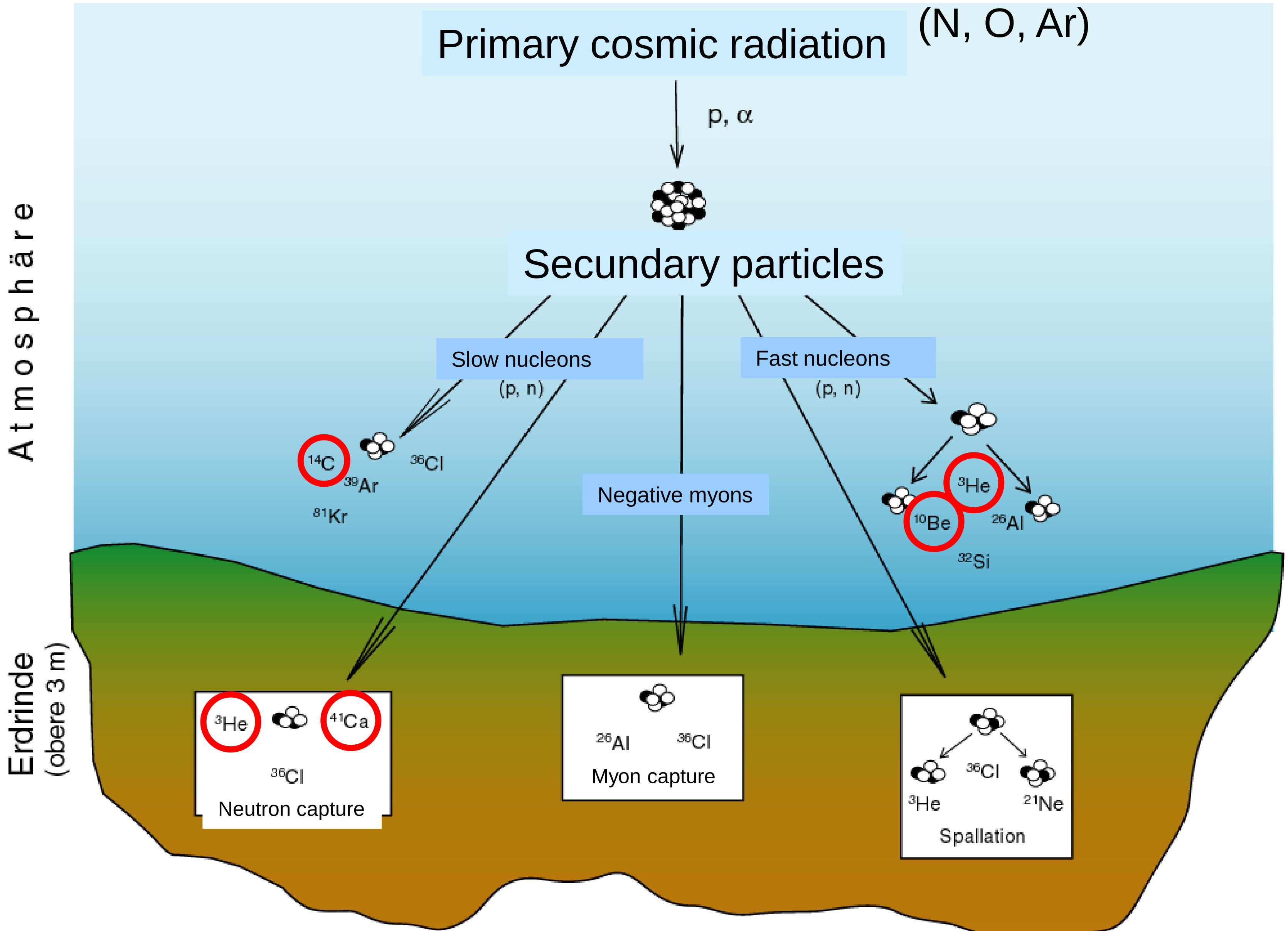
7.3.2 Analytics



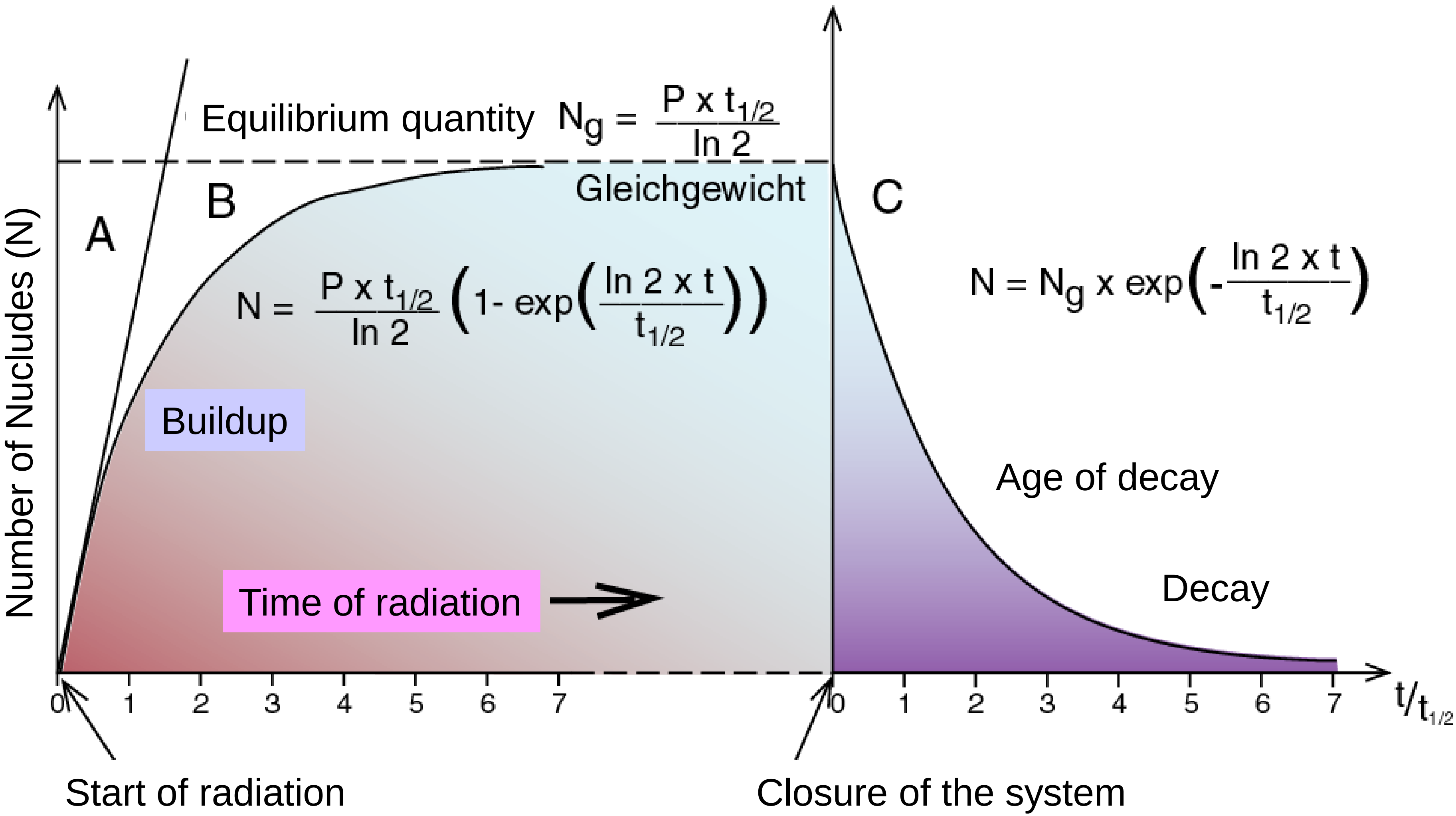
Assambly of a mass spectrometer

7.3.3 Selected methods for age determination

7.3.3.1 Cosmogenic nuclides: They were formed by radioactive decays which are produced by cosmogenic radiation which affects the atmosphere and earths surface.

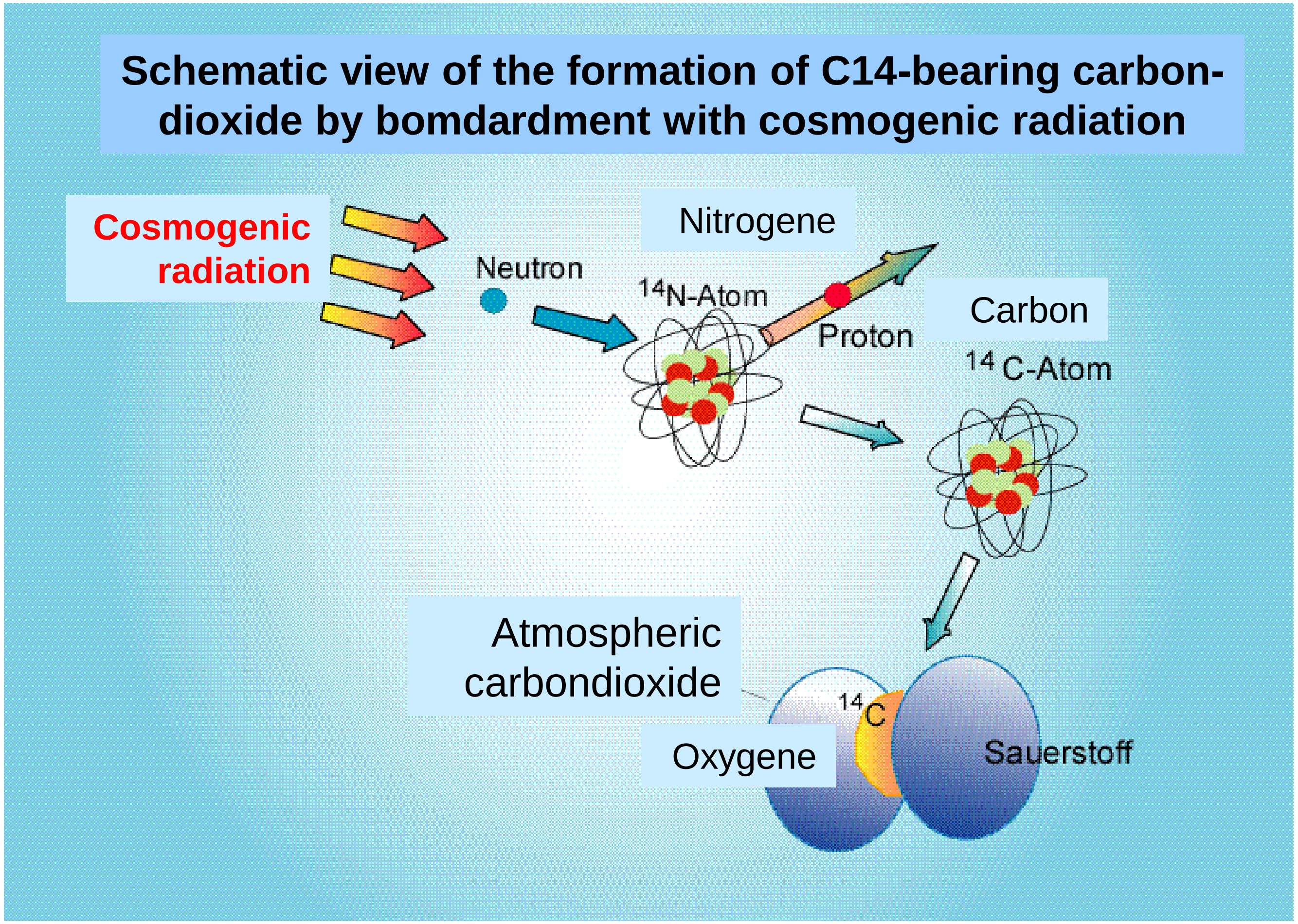


The amount of cosmogenic nucluides (N) which were formed in the atmosphere or in components of the earth surface rocks increase with time until an equilibrium is reached at a certain time, when formation and decay rates are the same. If a material becomes isolated from further radiation (closure of the system) an exponential decrease of the cosmogenic nuclides occurs with the time.



^{14}C dating

Formation: $${}_{0}^{1}n + {}_{7}^{14}N \rightarrow {}_{6}^{14}C + {}_{1}^{1}H$$

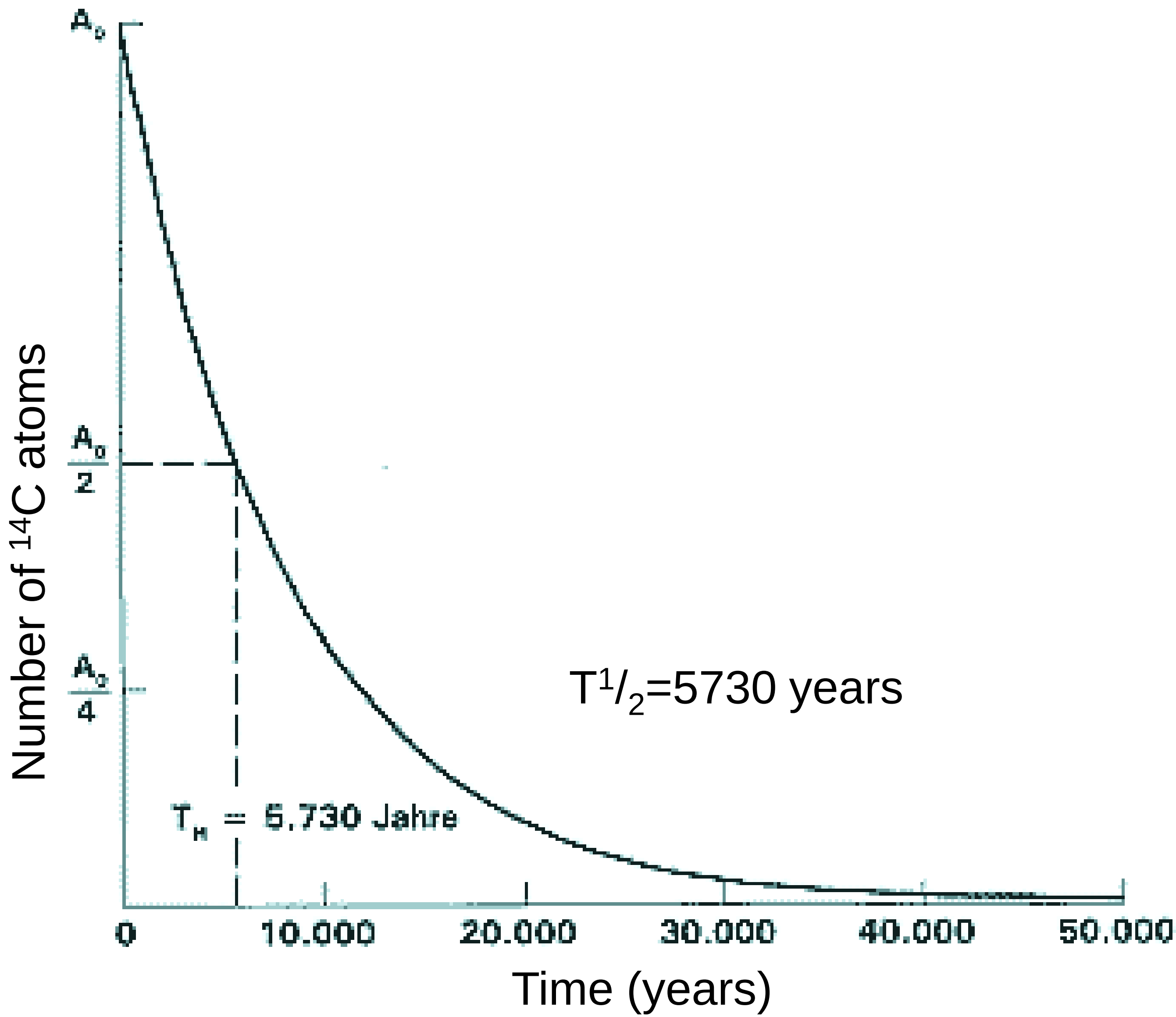


Decay: $${}_{6}^{14}C \rightarrow {}_{7}^{14}N + \beta^{-} + \nu + Q$$

ν = Antineutrino
Q = decay energy

Half-life time: 5730±40 years

The exponentiel decay of ^{14}C causes that very few ^{14}C remains in a sample after 50 000 years and the age determination becomes difficult or impossible.



The conventional ^{14}C ages

Conventional ^{14}C ages are given with respect to the following considerations and thus must therefore be calibrated. The calibration programm CALIB 8.0 can be dowloded for free from the Internet.

1. The reference year is the calendar year 1950 after Christus (BP = before present)

2. ^{14}C production rate has been considered as constant during the last 100.000 years.

3. The conventional ages are calculated with the wrong half-life time of Libby (5568 years with is 3 % to low).

4. The isotope fractionation $\delta^{13}C$ ist estimated to be $\delta^{13}C$ = -25 ‰

5. Possible reservoir effects are not considered

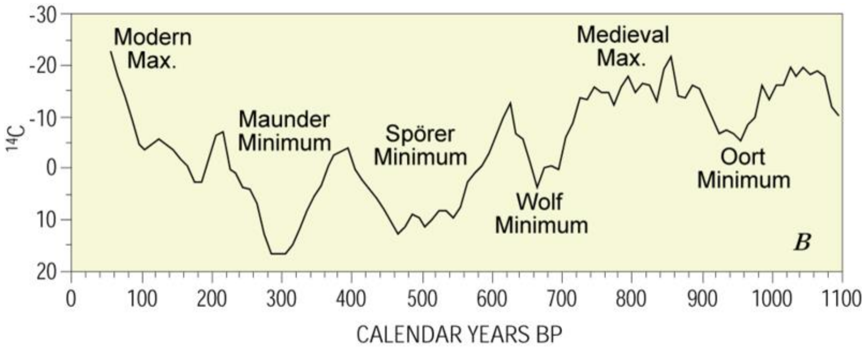
What causes variations in the atmospheric ^{14}C content?

1. **Changes in the production rate of radioactive carbon. Two factor are important:**

   a) The cosmogenic radiation is controlled and/or modified by the sun activity at different time scales of decades to centuries and millenia (=> Whiggles and DeVries-effects)

Variations of the relative atmospheric ^{14}C amount ($\delta^{14}C$):
The Maunder, Spörer, Wolf and Oort represent minima of solar activity.

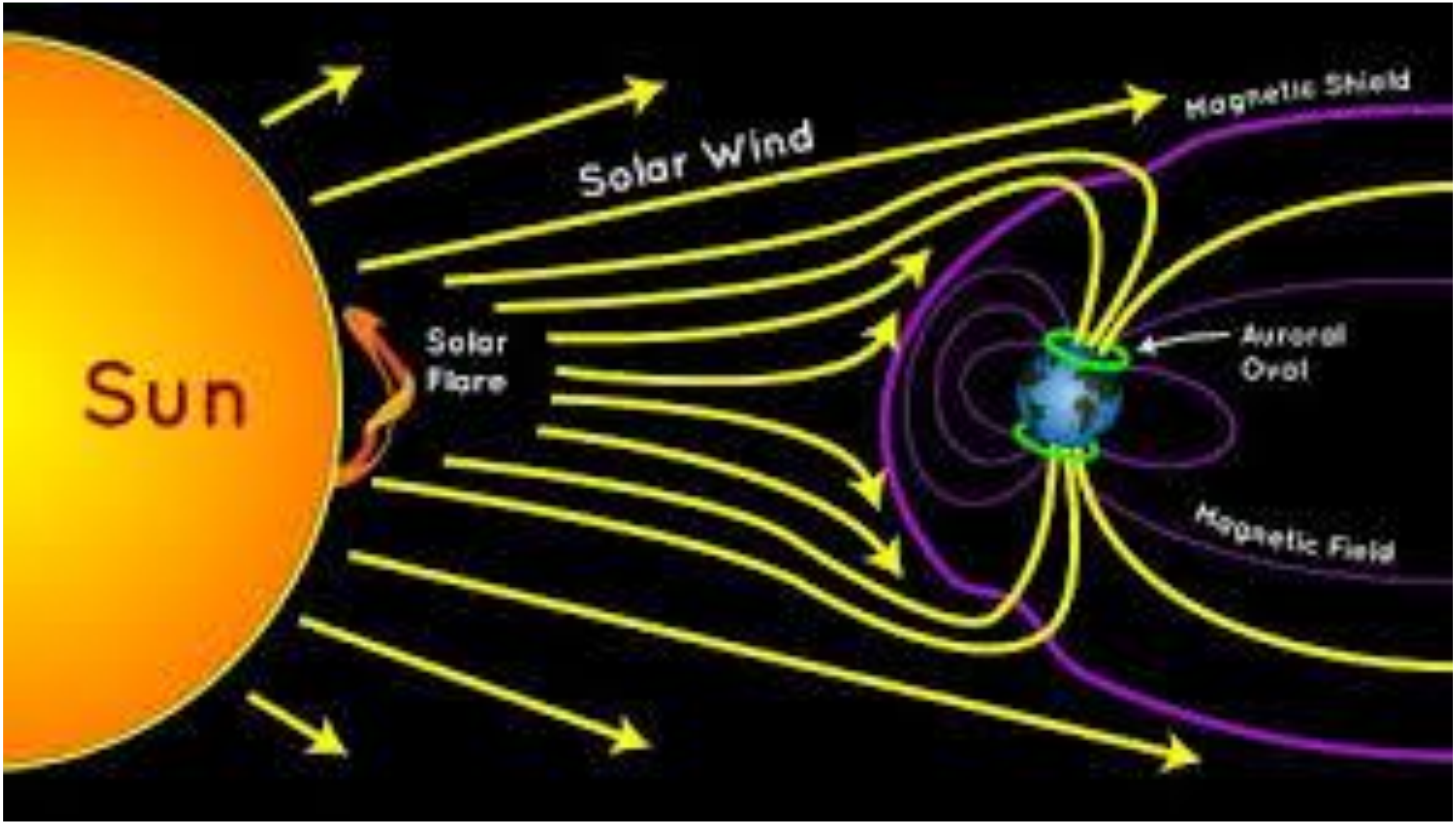
The modern maximum is produced by burning of old carbon reservoirs (oil, gas, coal)➔ De Vries (1958)



   b) The Earths magnetic field pproduces a shielding with respect to solar and cosmogenic radiation. Thus changes in the orientation and intensity of the Earths geomagnetic field influences also the production rate of ^{14}C

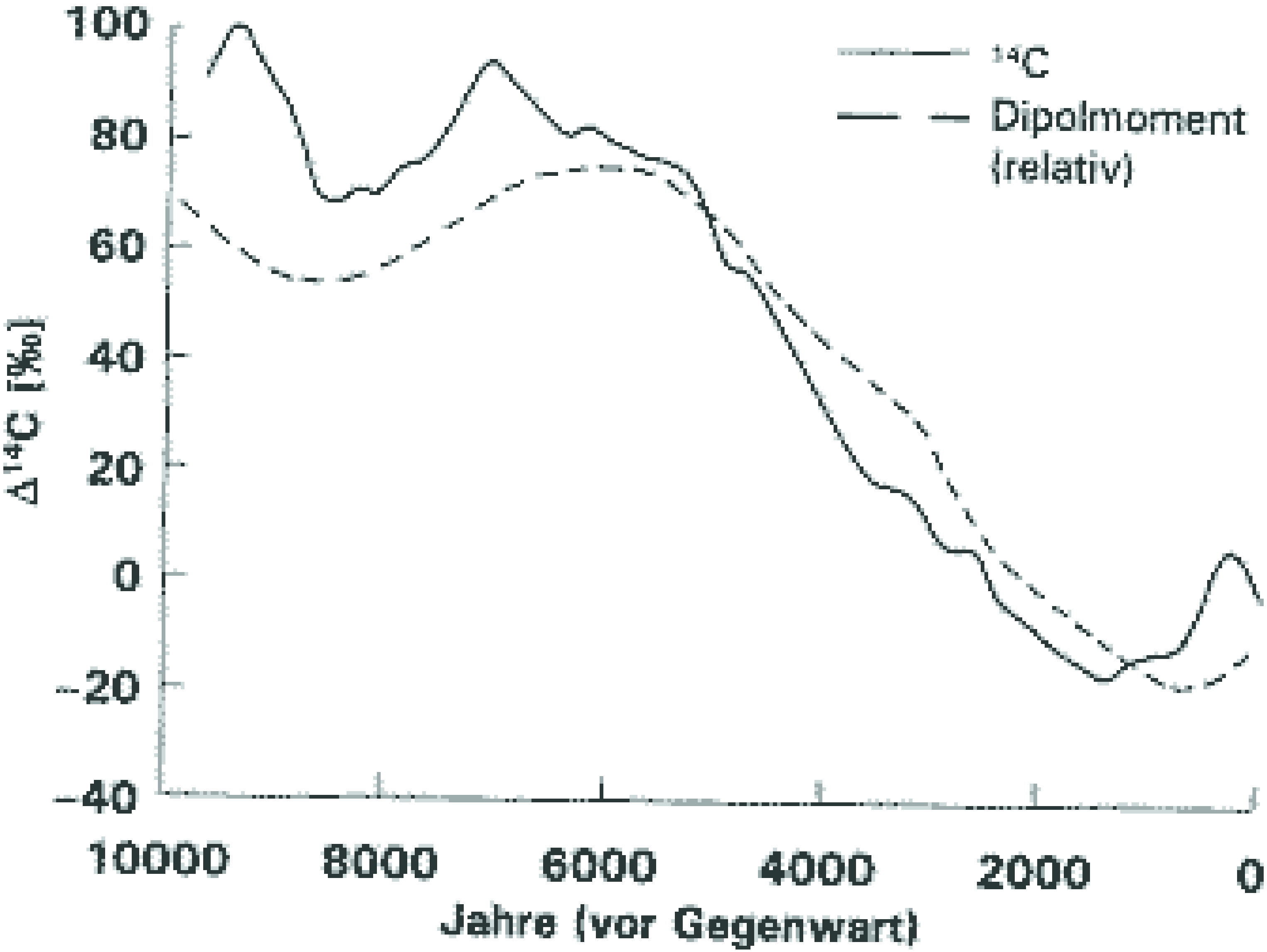
2. **Different distribution and variable input of „old" non-radiogenic carbon: for example from volcanic emissions and/or outgassing of deeper water from oceans**

The solar wind deforms the magnetic field around the Earth and protects the Earth against „solar stripping“



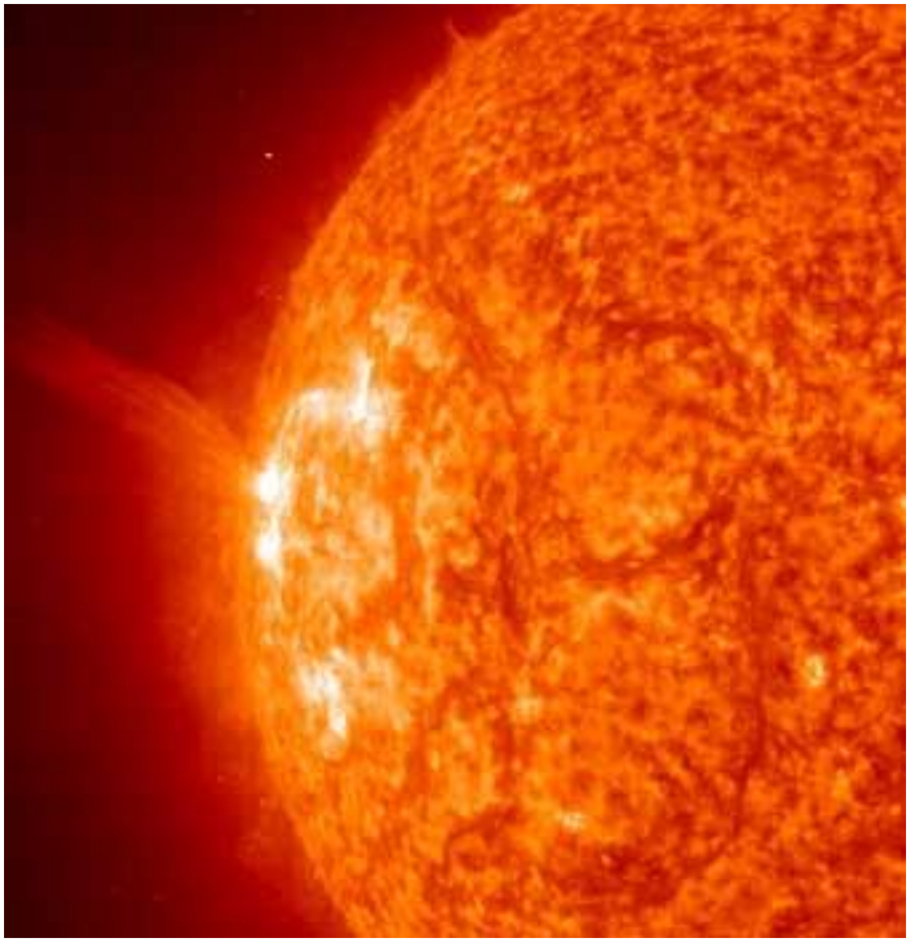
The influence of the earths magnet field

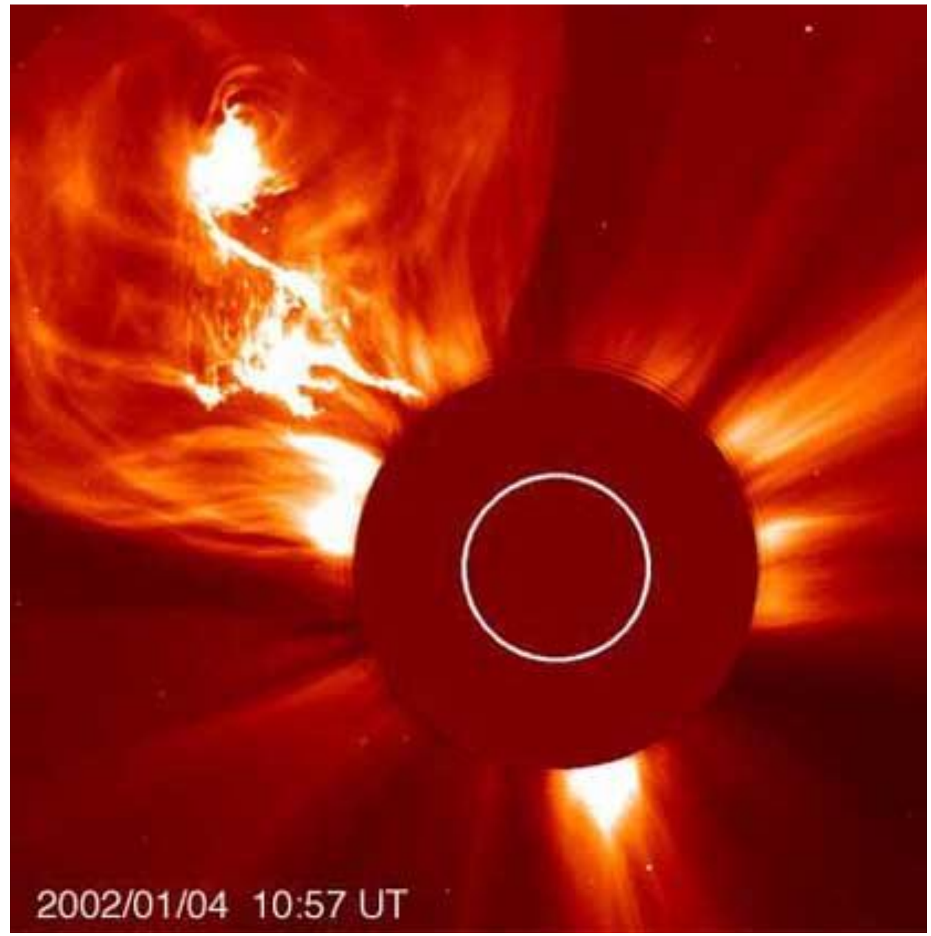
Struvier et al. 1991



Influence on ^{14}C production rate:

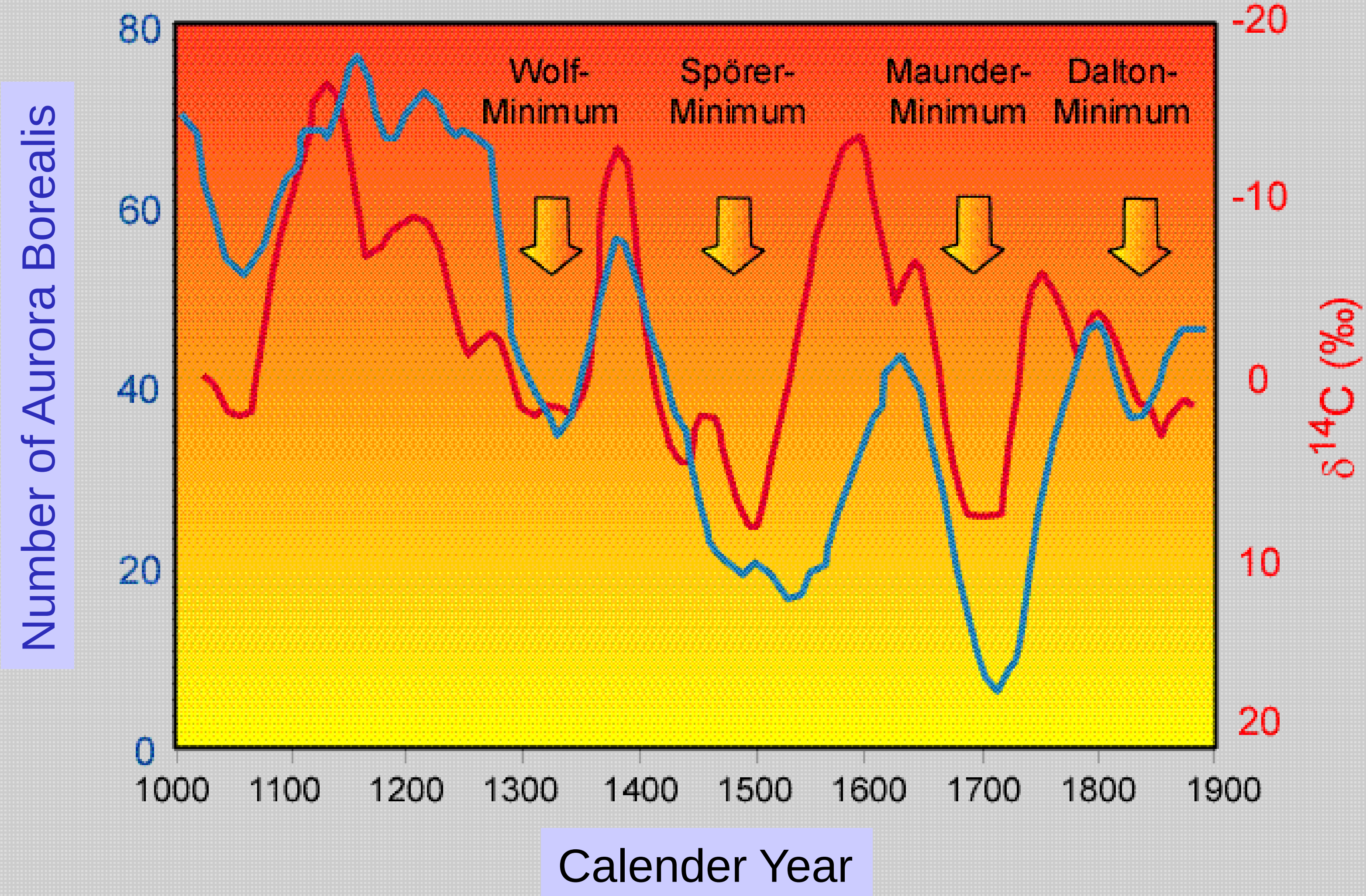
Sun spots are related to changes in the sun energy





Solar eruption in April 2002

Comparison of the number of observed Aurora Borealis and $\delta^{14}C$ values determined from tree rings of known ages



2. Different distribution and/or variable input of „old“ non-radiogenic carbon ➔ reservoir effects

➔Heterogeneous distribution of newly formed cosogneic

➔Contribution of CO_2 from „old carbon reservoirs“:

- e.g. contamination with old CO_2 from volcanic emissions

Tephra eruption

Mt. St. Helens, May 1980 eruption

Volcanism

- Contamination by dilution of „ol eas)

- „old“ CO_2 (^{14}C-frei) from deep oceans

  ➔ Reservoir effects could be between 200 and >1600years.

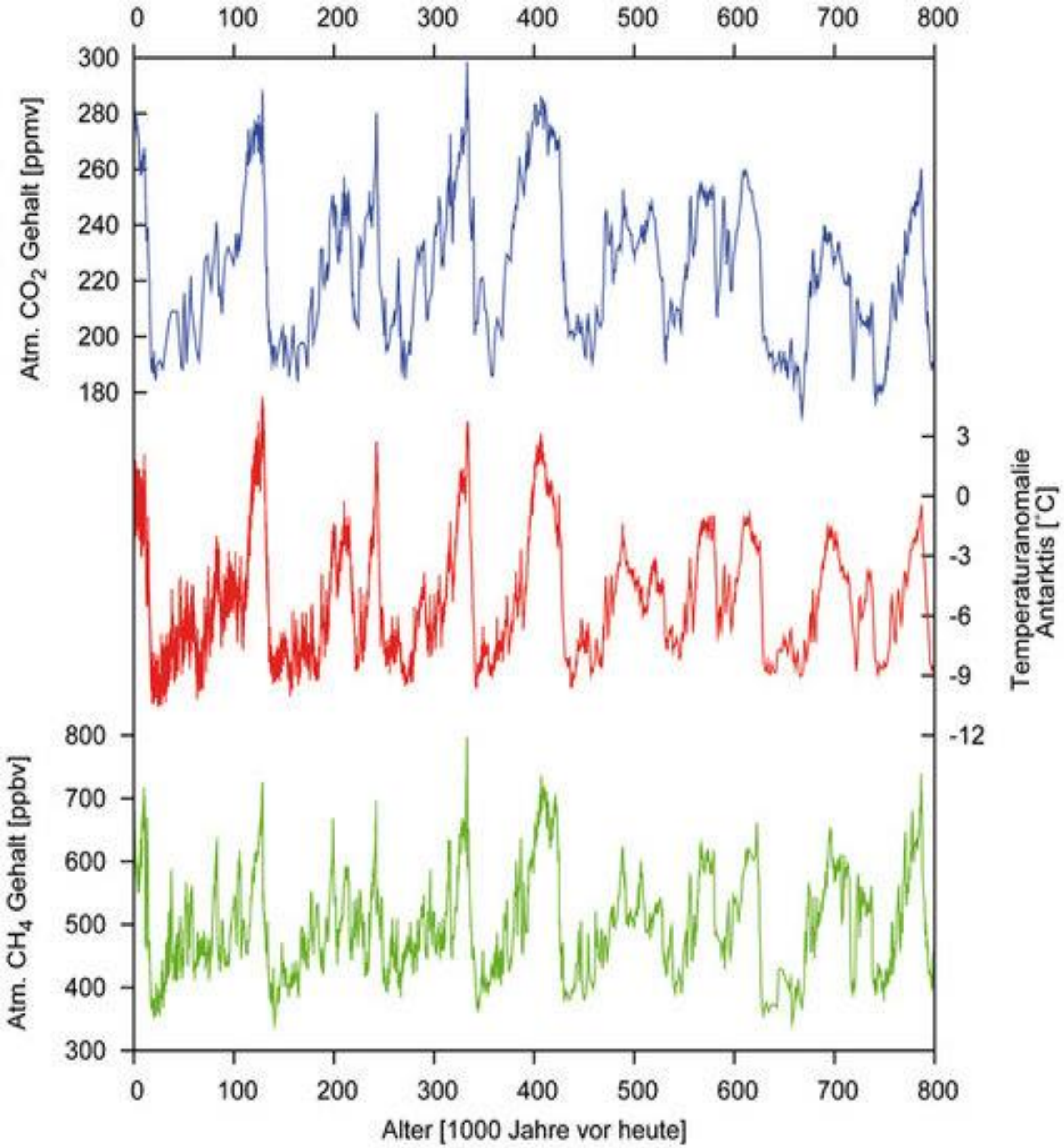
Changes in the global ^{12}C volume in the atmosphere:

- Disolution of CO_2 in the Oceans increases with decreasing temperature.

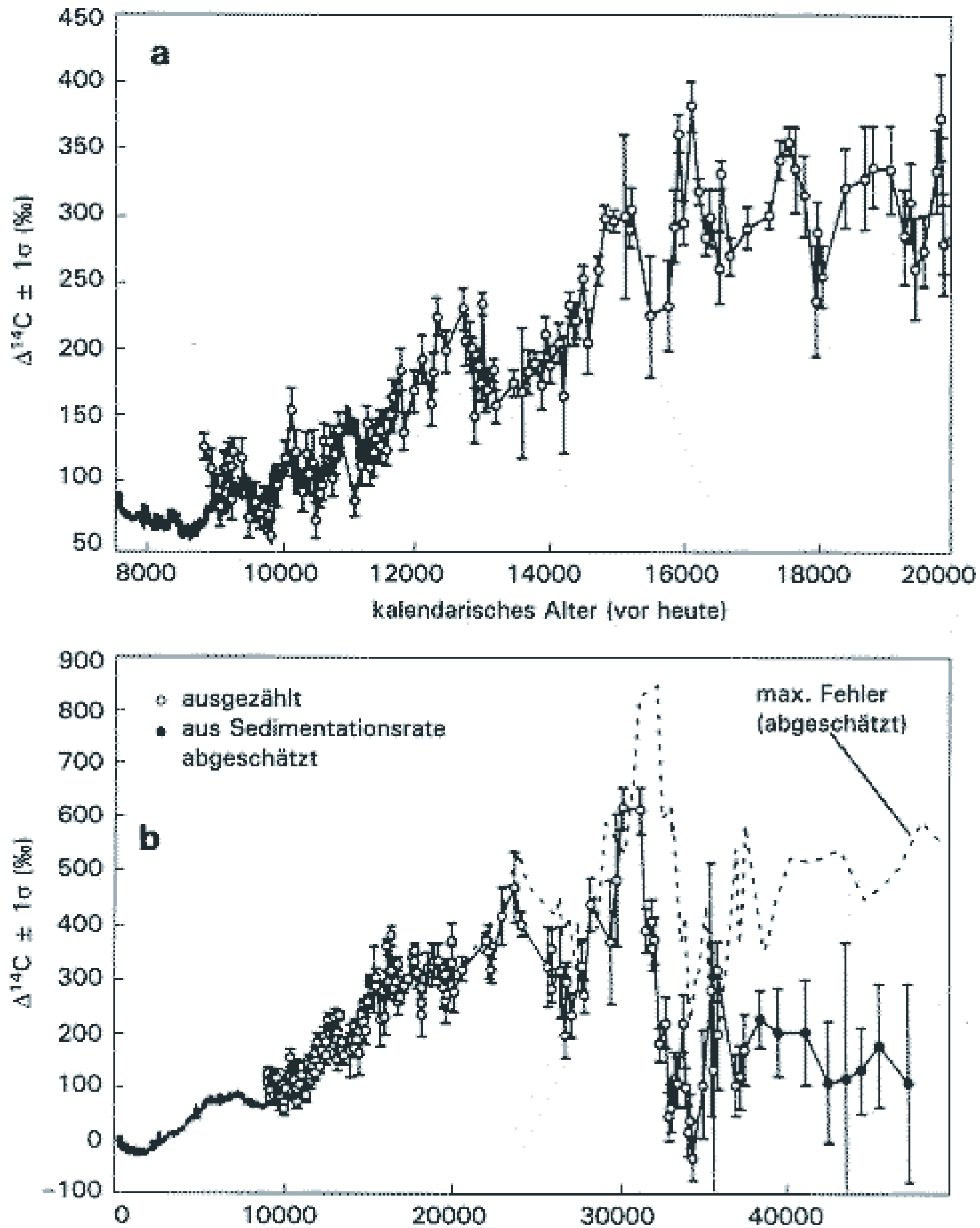
  ➔during golbal cooling the atmospheric CO_2 levels decrease

  ➔ Thus calibrated Glacial radiokarbon ages are about 2000 to 3000 years younger than uncalibrated ages .

- A very strong cahnge in the atmospheric $^{14}C/^{12}C$ ratios occured during the Younger Dryas cold period



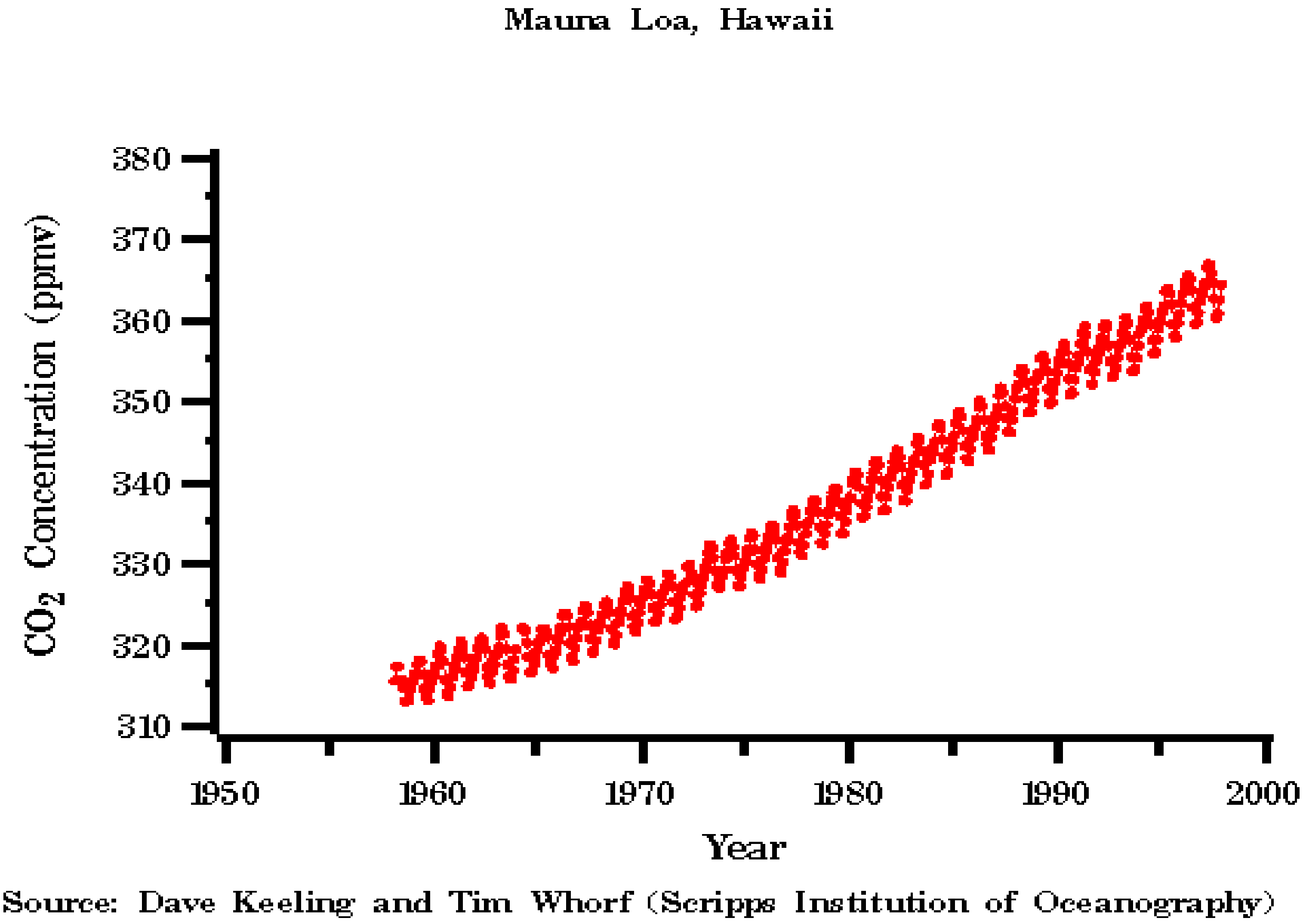
During the Last Glacial the atmosphere was characterised by relatively high and variable ^{14}C concentrations compared to the Late Holcene and present. This is due to the general low CO_2 concentration wwhich provides less dilution of the radionegic carbon.



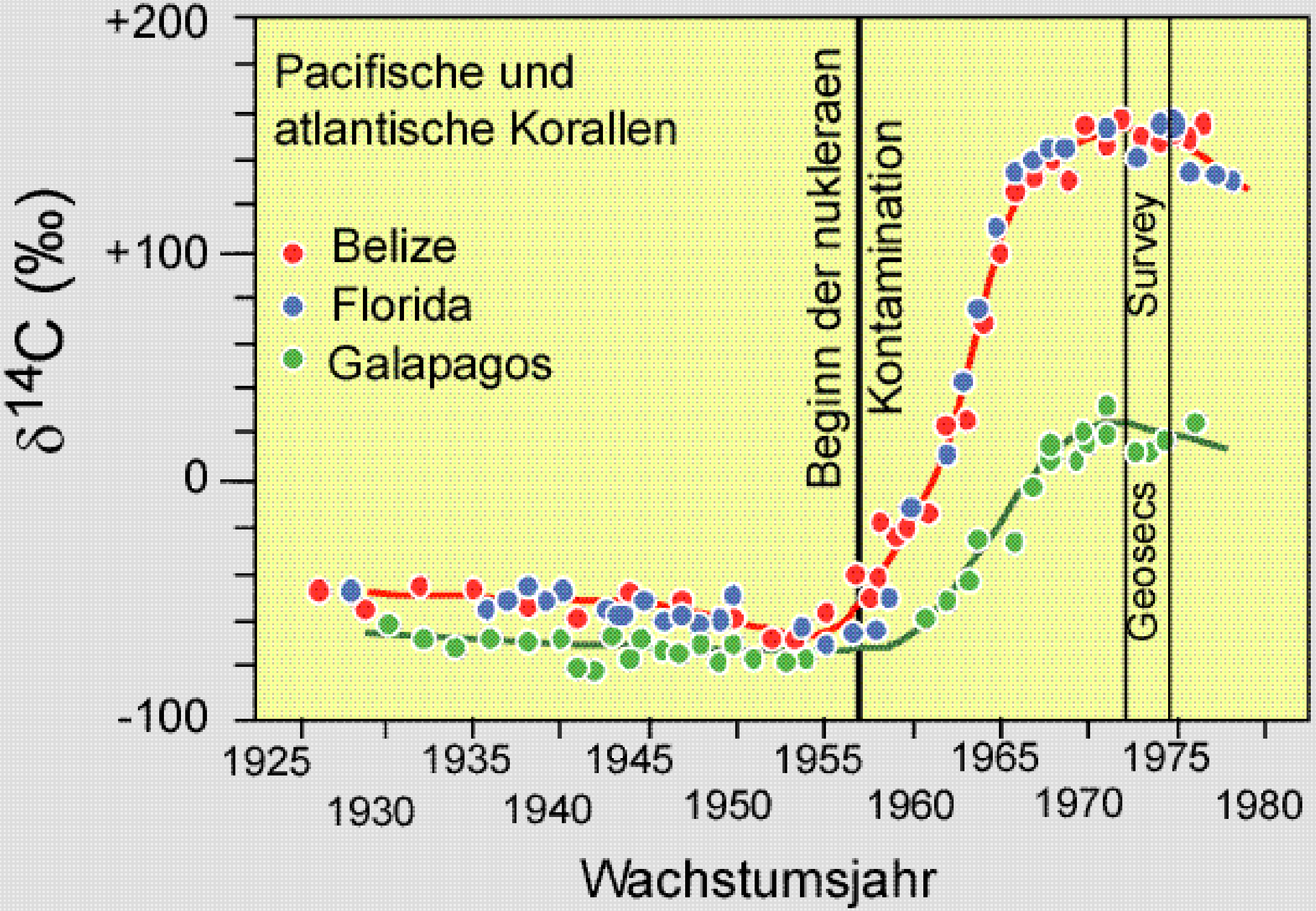
Calendaric Age (before present)

Kitagawa & van der Plicht (1998a)

The anthropogenic increase of CO_2 is diluting the relative content of ^{14}C in the earths atmosphere. Therefore uncalibrated ages are to low (Suess-Effekt).



Der Kernwaffeneffekt:

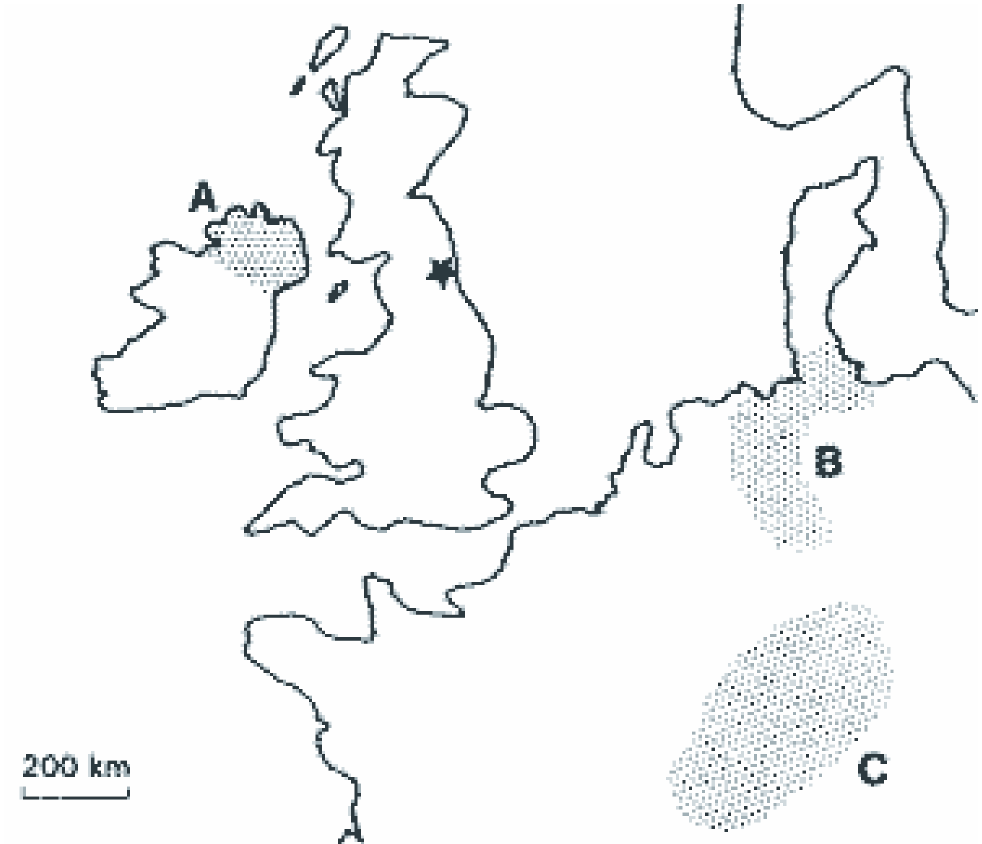


$$\delta^{14}C = \frac{(^{14}C/C)_{Probe} - (^{14}C/C)_{Std}}{(^{14}C/C)_{Std}} * 1000$$

Calibration of radiocarbon ages:

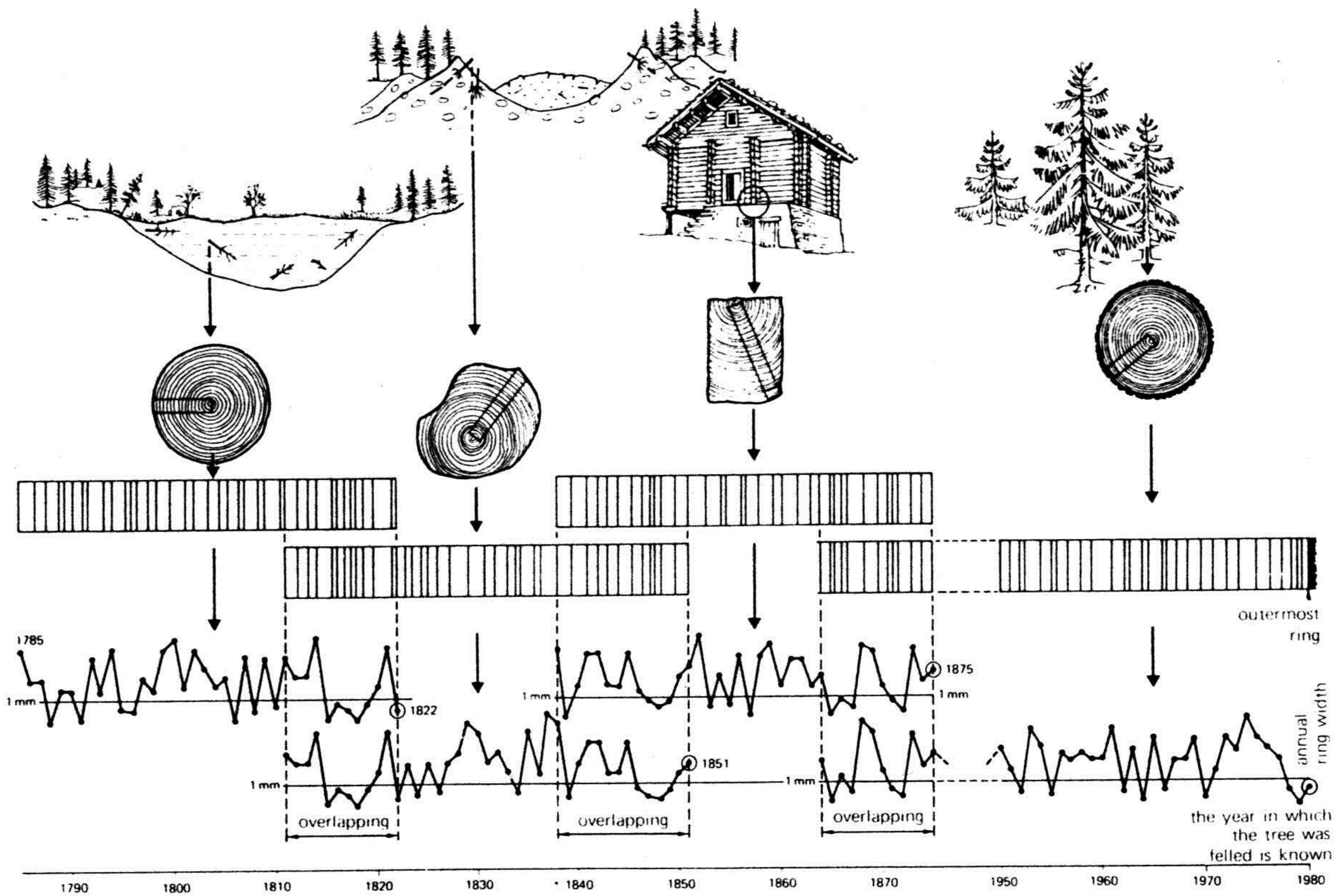
For the calibration of ^{14}C-ages carbon-bearing material is used from records which can provide an independent absolute age. For example tree ring chronologies (tree ring counting) and warve chronologies and/or independent U/Th ages

Areas in Europa from where oaks has been used for dendrochronological calibrations.



Pilcher et al. 1984

Tree ring chronologies used for calibration curves

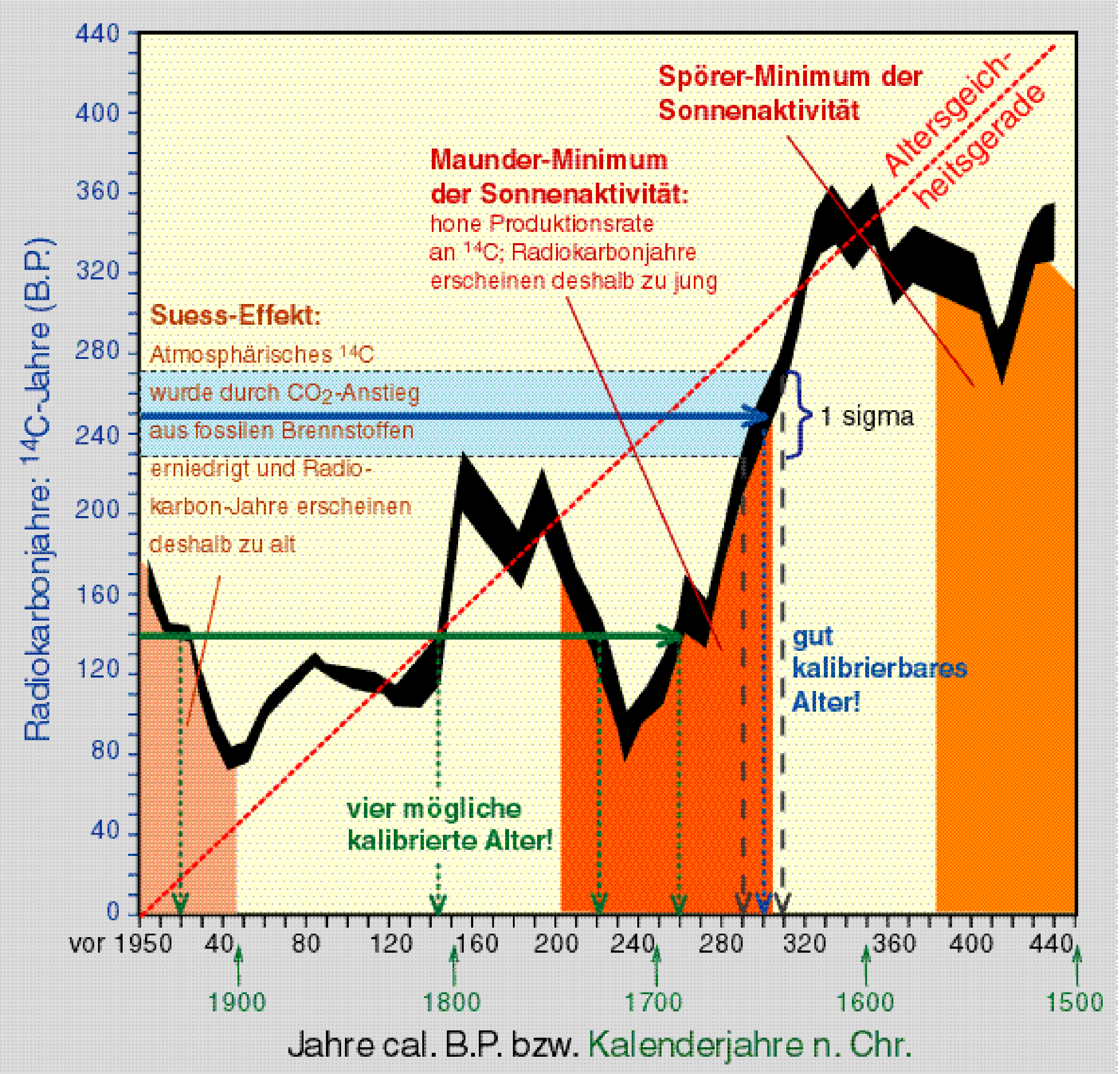


Calibration curve for ^{14}C ages

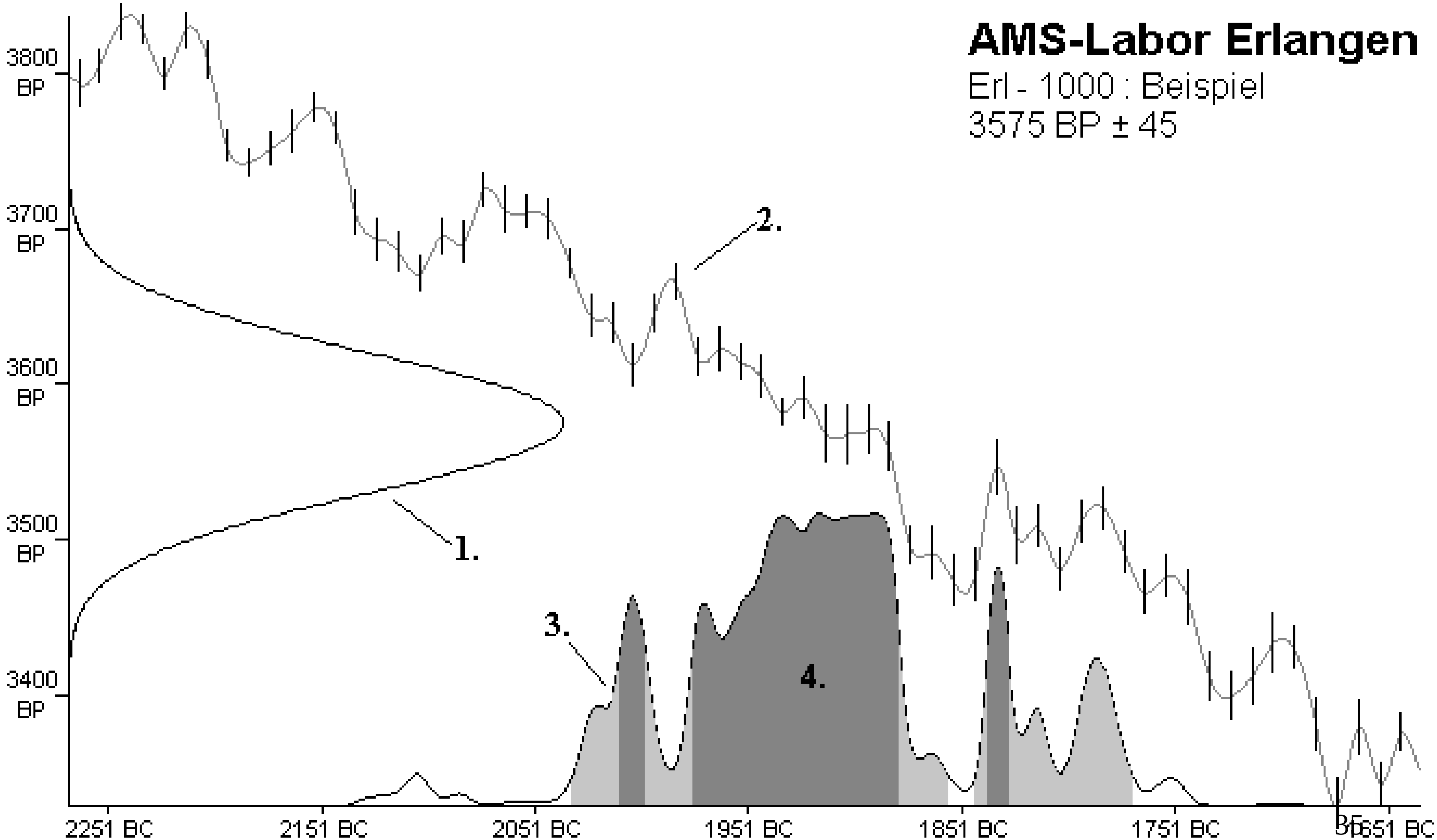
Beziehung zwischen konventionellem ^{14}C-Alter und Kalenderjahren, gemessen an Baum-jahresringen der Douglastanne.

Industrial CO_2-increase (Suess Effect)

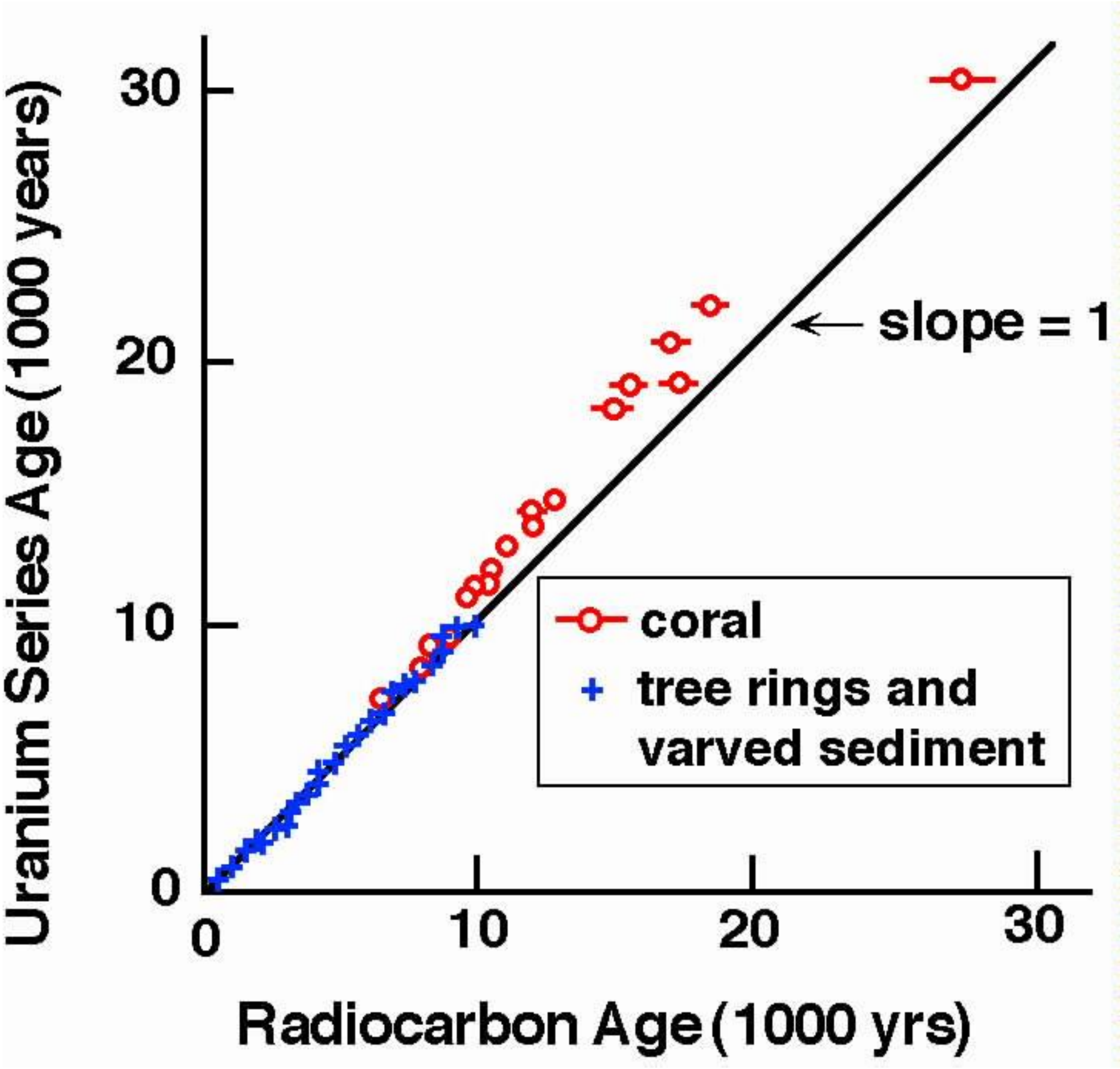
Variation in the initial ^{14}C productuion rate due to changing solar activity Sonneaktivität (Dalton-, Maunder- und Spörer Minimas)



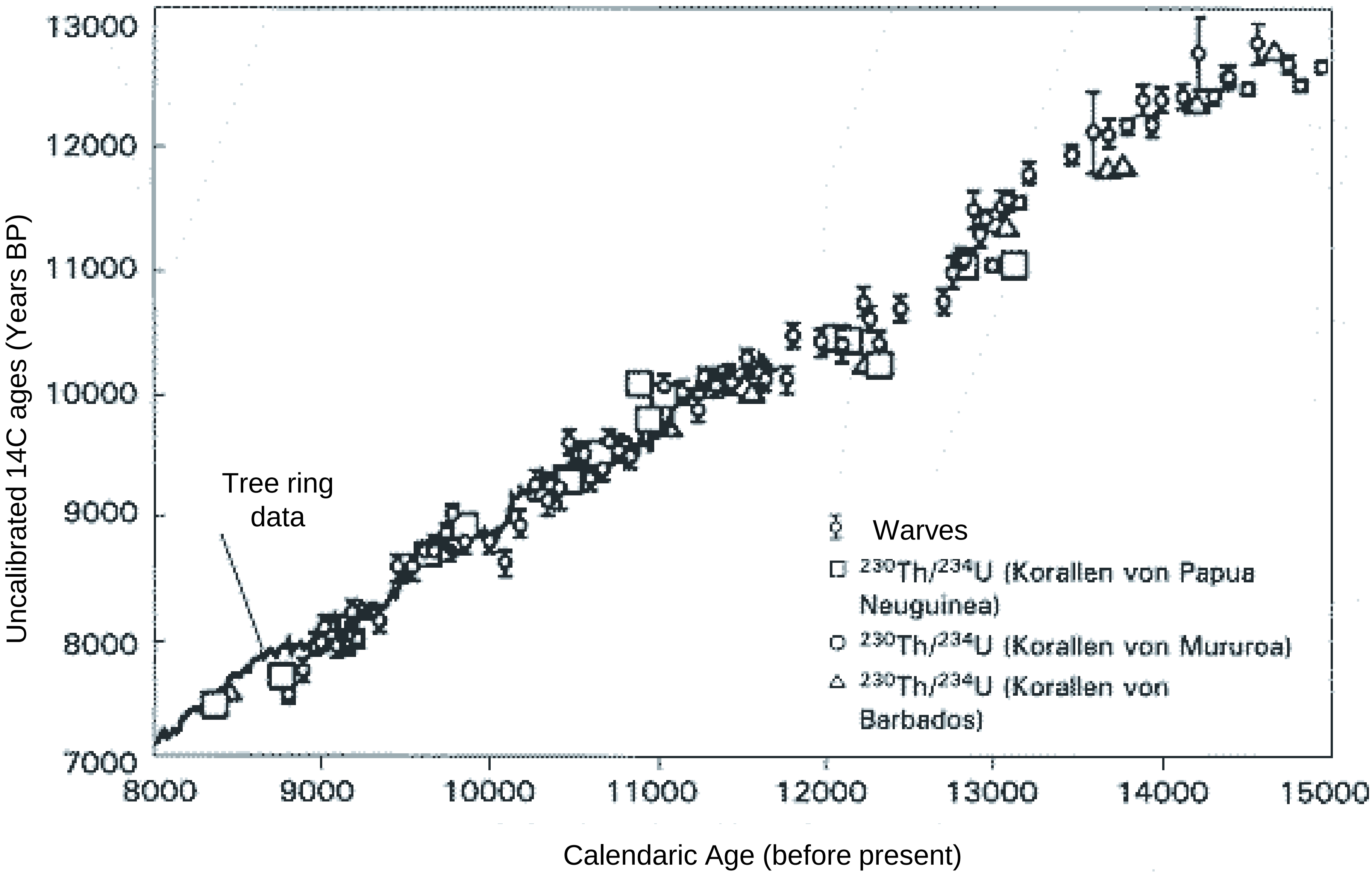
Example of a ^{14}C calibration



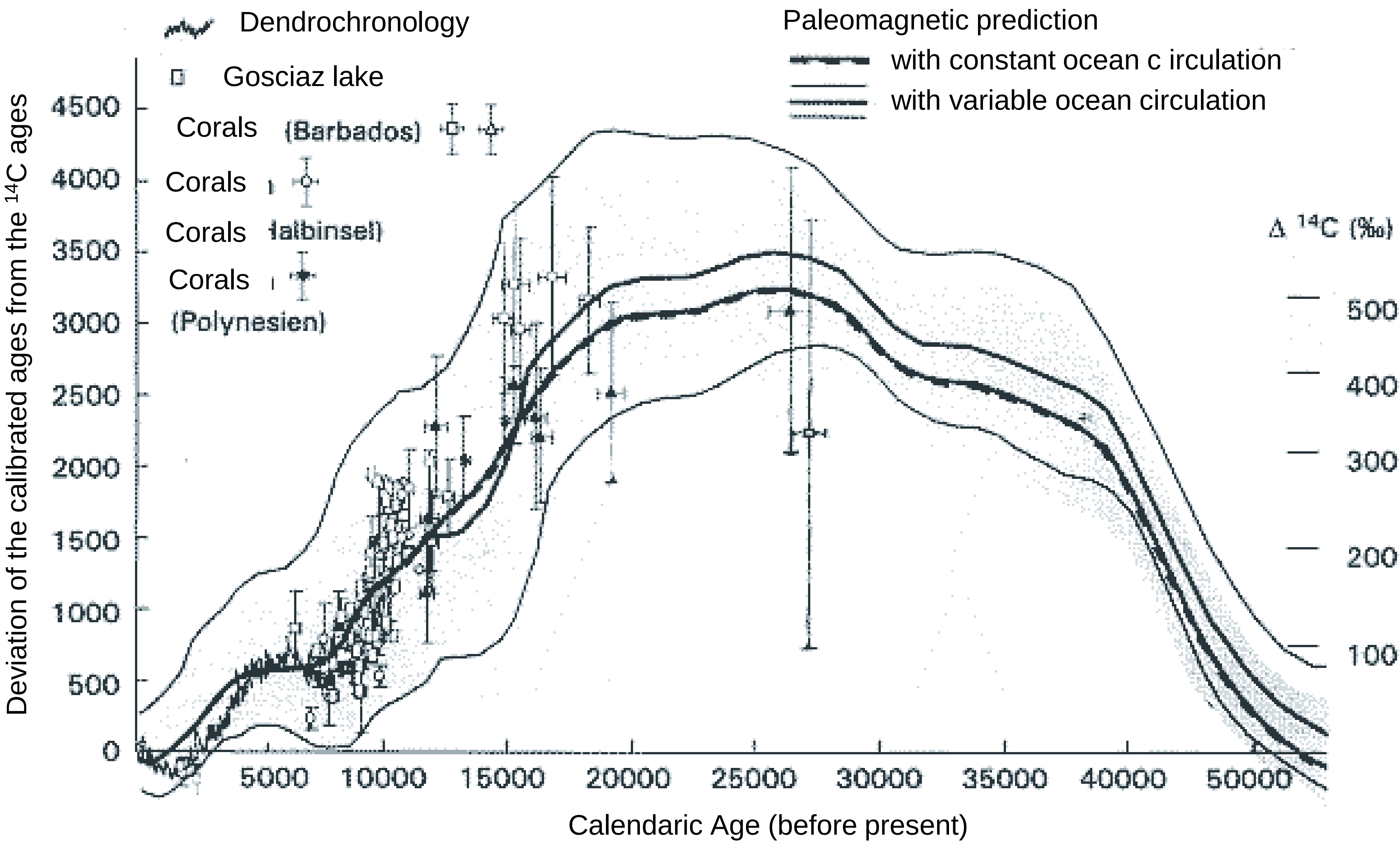
^{14}C calibration curve



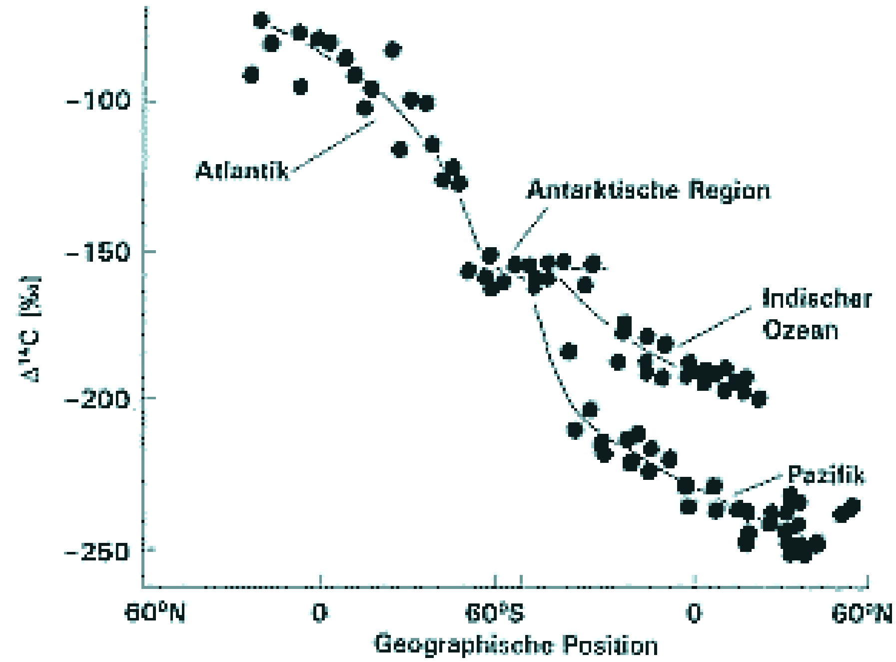
Radiokarbonages compared to ages of warves and tree rings (Edwards et al. 1993) after Kitagawa & van der Plicht (1998). $^{230}Th/^{234}U$ ages of corals are also compared after Bard et al. (1990).

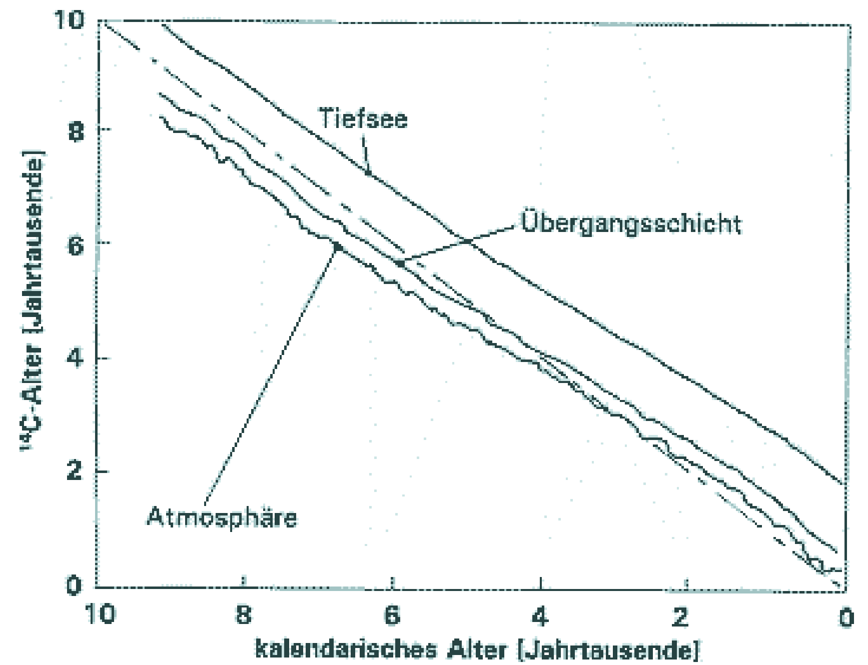


Vergleich der paläomagnetisch vorhergesagten ^{14}C-Isotopenverschiebung (nach Laj et al. 1996) mit dendrochronologischen und Th/U-Daten



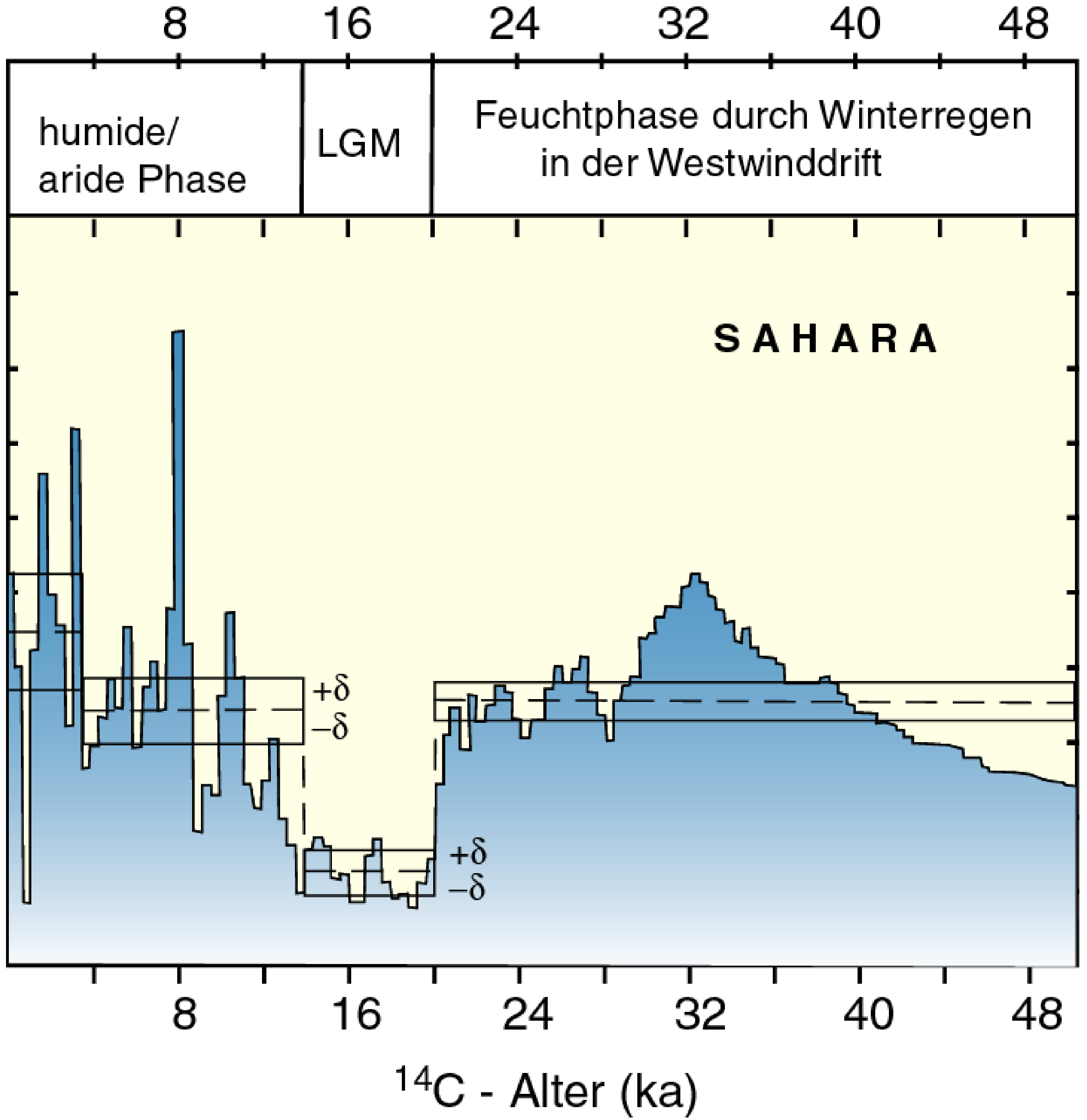
Distinct ages of marine waters due due different mixing processes of large oceanic water masses.





Stuiver et al. 1986

Frequency distribution of ^{14}C ages in artesic ground water probes from the Sahara *(Sonntag 1980)*



7.3.3.2 Nobele gases formed by radioactive decay

^{40}K ➔ ^{40}Ar (>10 000 years) in potassium-bearing vulkanic glasses and/or minerals

^{4}He from radioactive decay of U-Th series (10 ka – 100 Ma)

Potassium isotopes

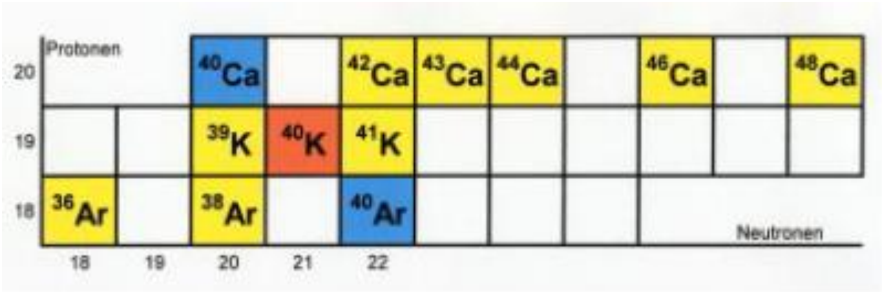
^{39}K (93,2581%)

^{40}K (0,01167%) radioactive

^{41}K (6,7302%)

The K-Ar method and the Ar-Ar-method can be applied at K-bearing components (>1 wt.% K_2O) of rocks and minerals, like biotite, muscowite, phengite, paragonite, amphibol, Alkalifeldspar or vulcanic glasses.

K-Ar method



- Decay:

$^{40}K \rightarrow ^{40}Ar$ (β^- decay, electron capture)

$^{40}K \rightarrow ^{40}Ca$ (β^+ decay)

Half-life time: $t_{1/2}$ (^{40}K) = $1.250 \cdot 10^9$ a

Depending on the potassium content it is even posible to determine Holocene ages

- Problems:

- bad Ar-retentivity of some minerals
- Temperature sensitivity of the system
- Excess–Ar
- Ar-loss
- missing posibility to correct for initial Ar

$^{40}Ar_{rad}$ - ^{39}Ar method

The major isotop $^{39}K_{stabil}$ of potassium-bearing minerals is transformed into the ^{39}Ar isotope by radiation of the probe with fast neutrons. This ^{39}Ar which was induced by radiation proportional to the orgiginal postassium content of the mineral. From this the $^{40}Ar_{rad}/^{40}K_{stabil}$ ratio and the age of the probe can be deduced.

Advantage: Both noble gases can be released from the probe during stepwise heating and can be meassured simultaneously in a mass spectrometer.

Appropriate minerals for the K-Ar- and Ar-Ar-Methods

Note: most minerals have different closure temperatures and different potassium content

Feldspars: especially alkalifeldspars

Further silicates: Leucite, Nepheline

Micas: e.g. Biotite, Muscowite

Further sheet silicates : Chlorite, Illite

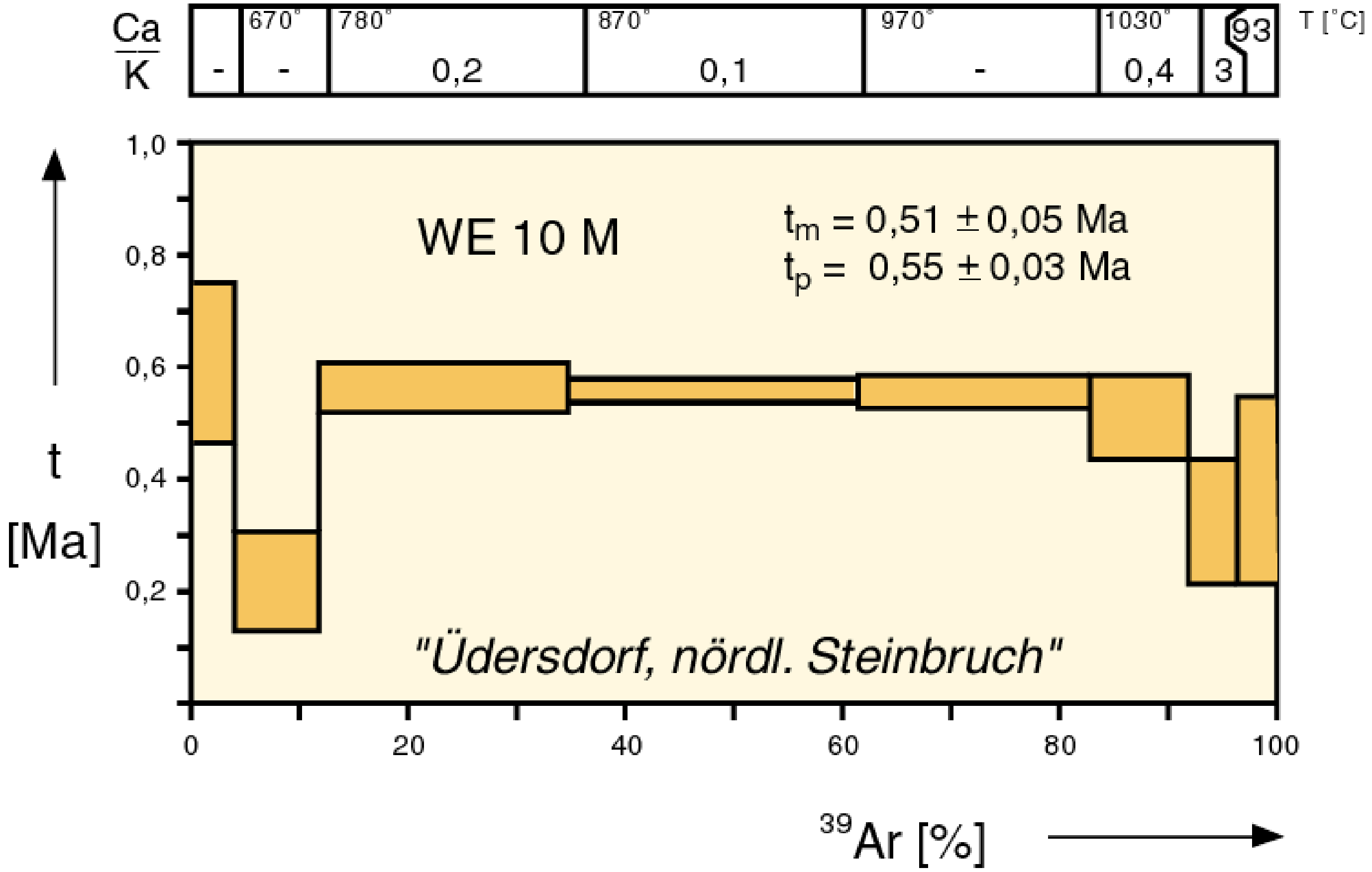
Hornblenden: Actinolite, Na-Amphibole

Pyroxene: difficult due to fue K

Wasserfreie Vulkanite: insbesondere Gläser

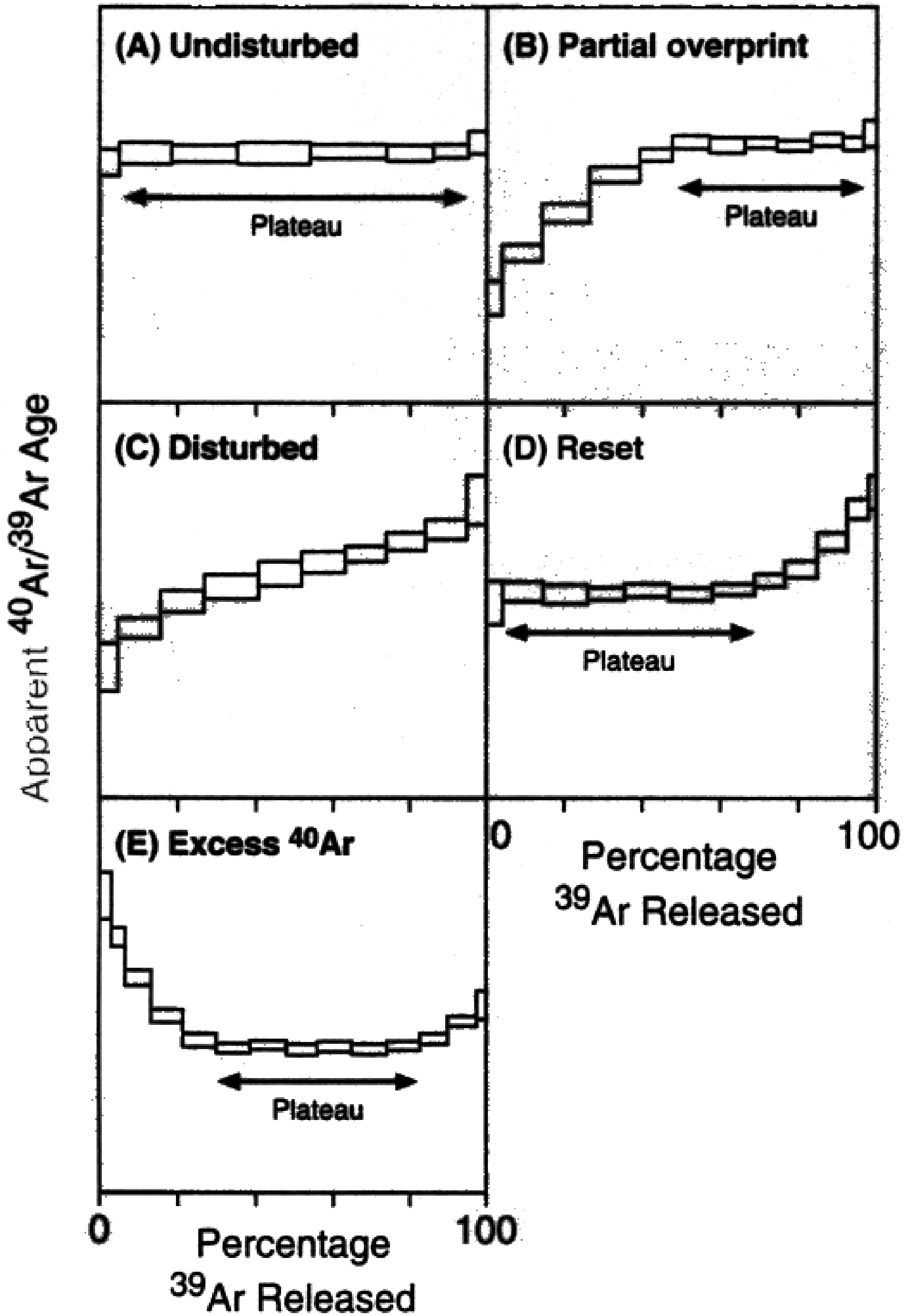
Whole rock: difficlut due to Ar-loss

K-Ar and Ar/Ar ages

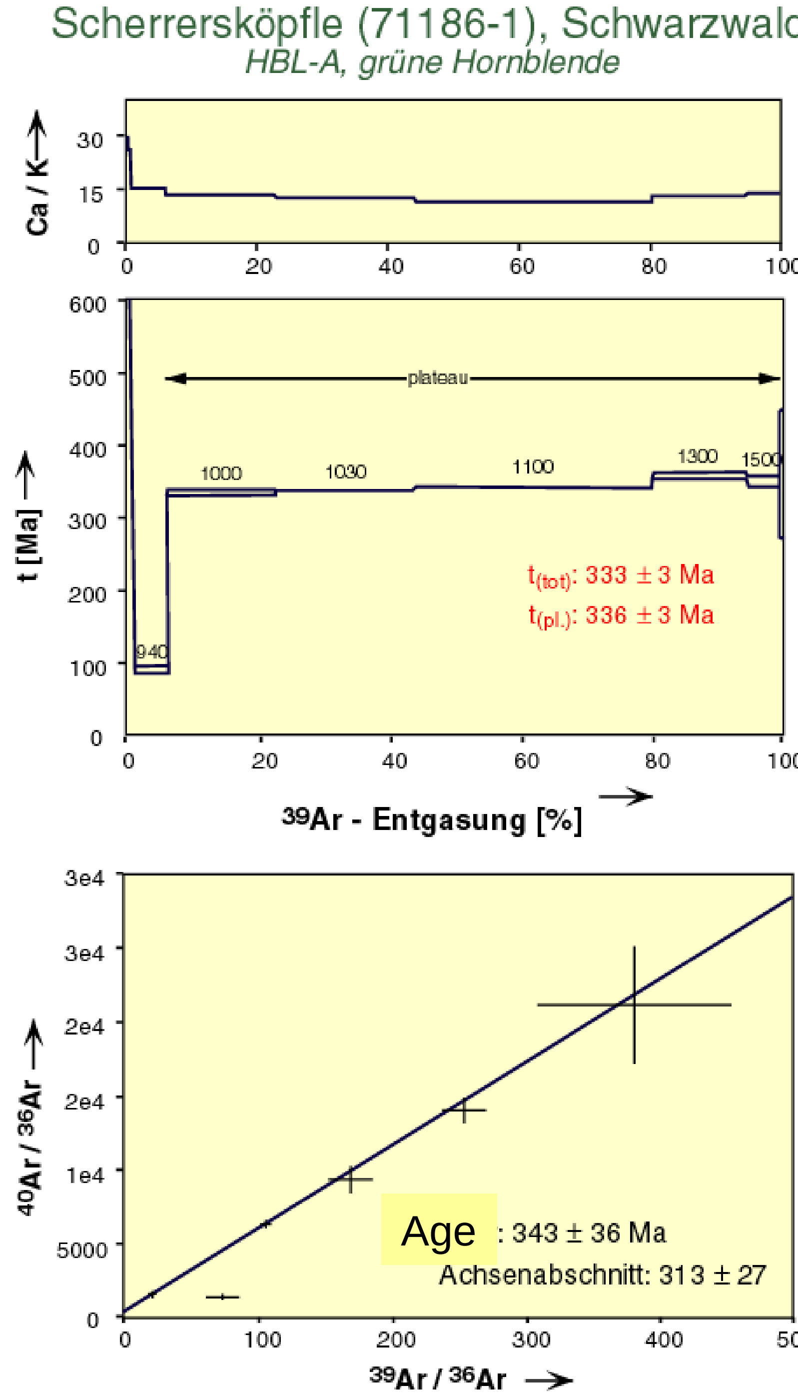


$^{40}Ar/^{39}Ar$ age spectra during stepwise heating of the ground mass of a basanite (volcanic rock) from the western Eifel in Germany. The plateau age (t_p) correspond to the conventionel K-Ar age(t_m)

^{40}Ar-^{39}Ar age spectra during stepwise heating of argon-bearing minerals. Only plateaus are able to indicate confiable ages:



Example of a Ar-Ar age of hornblende minerals of a granitoid of the Black Forest, Germany



Hradetzky (1989)

Reasons for Ar-loss

- Bad Ar retentivity of some minerals within the low-p and low-T range
- Temperature increase due to a prograde metamorphism
- Hyrothermal alteration and weathering of minerals
- Mechanical stress of minerals in rocks
- Radiation damages

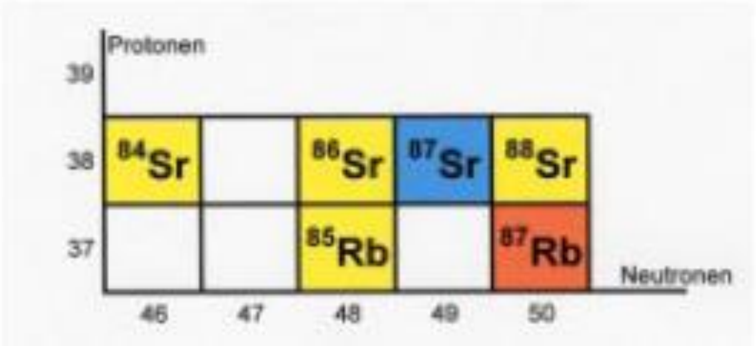
Rb-Sr method

Rb:	^{85}Rb:	72.1654%	**Sr**:	^{88}Sr:	82.53%
	^{87}Rb:	27.8346% rad ➔		^{87}Sr:	7.04%
				^{86}Sr:	9.87%
				^{84}Sr:	0.56%

$^{85}Rb/^{87}Rb = 2.59265$

$^{86}Sr/^{88}Sr = 0.1194$

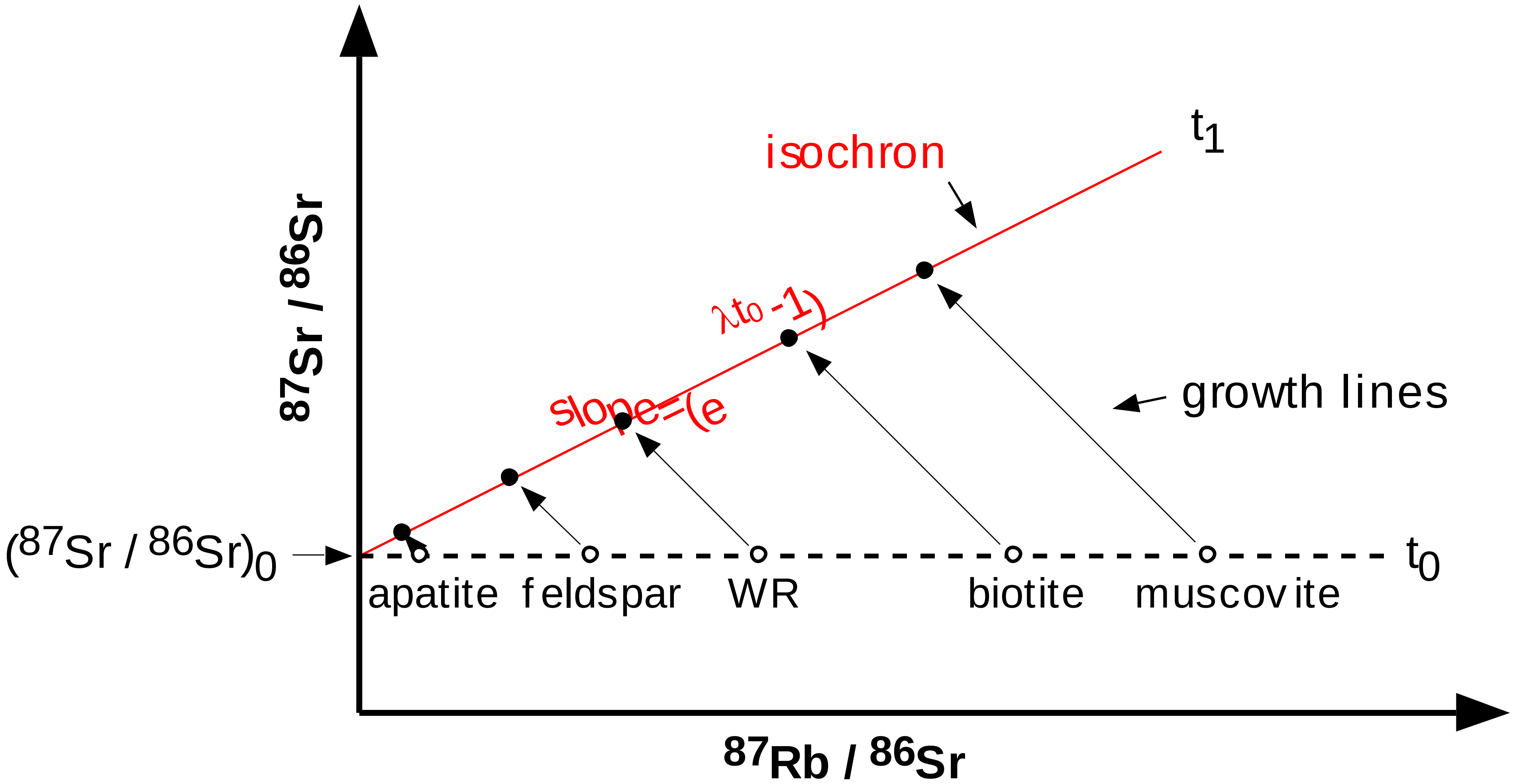
$^{84}Sr/^{86}Sr = 0.056584$



$\lambda = 1.42 \times 10^{-11} a^{-1}$

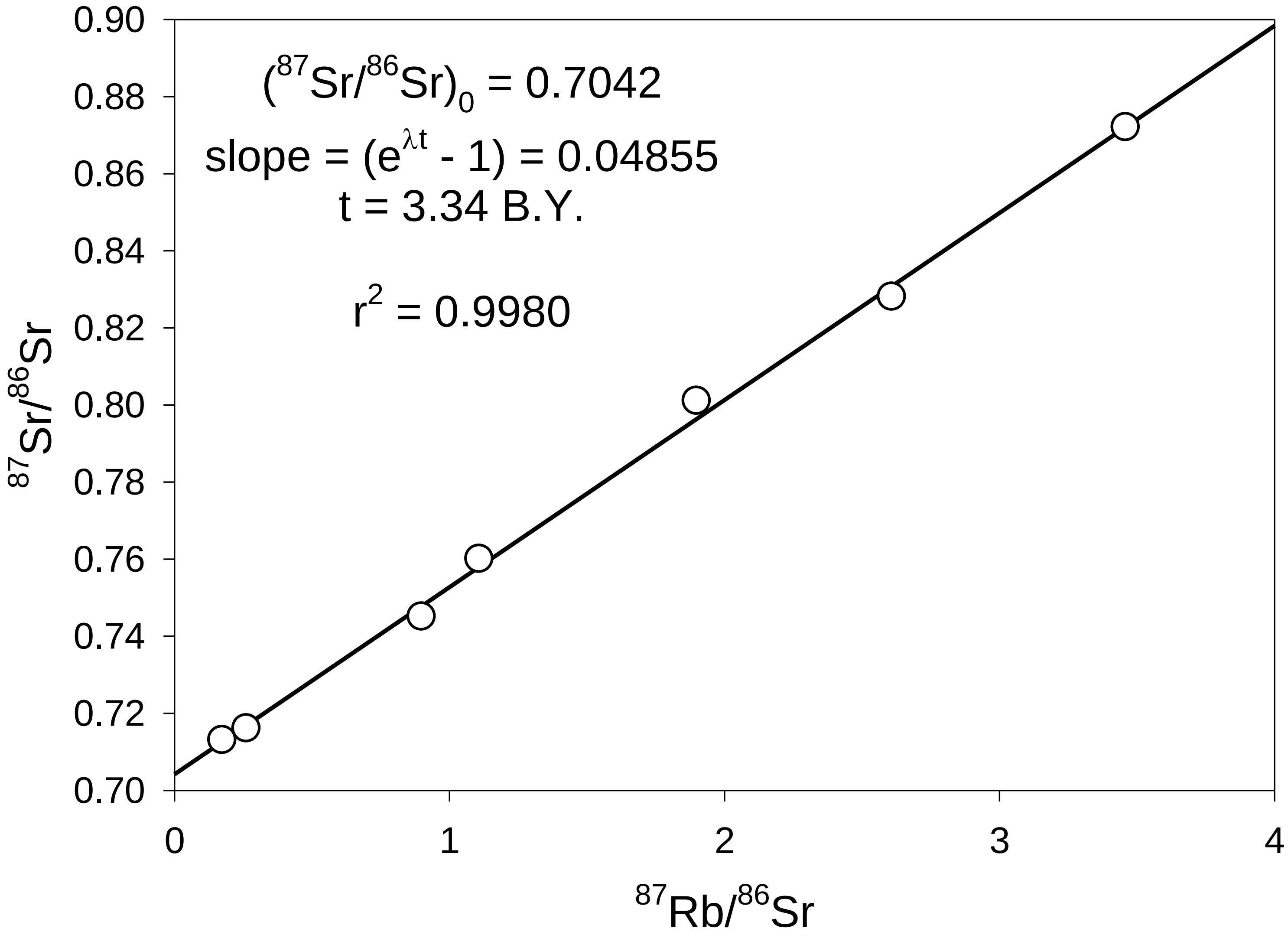
$t_{1/2}(^{87}Rb) = 48.8 \times 10^{9}$ a

$^{87}Rb \rightarrow {}^{87}Sr + \beta^- + \bar{\nu} + E$

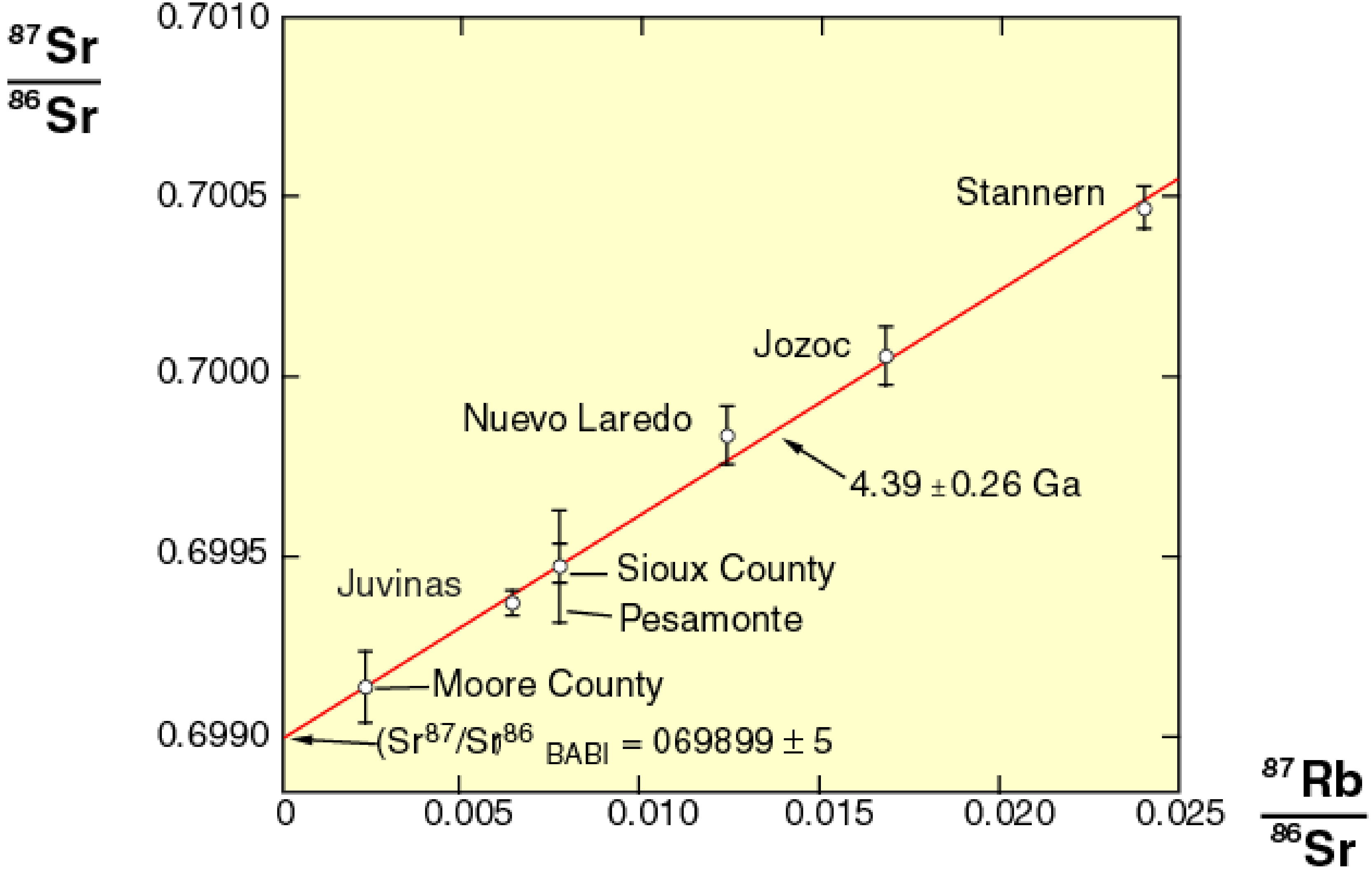


Rb-Sr isochron diagram (Nicolaysen 1961) for minerals (e.g. apatite, feldspar) and a bulk granite sample (Geyh & Schleicher 1990)

Rb-Sr isochron for a serious of meteorites, which has been formed at the same time

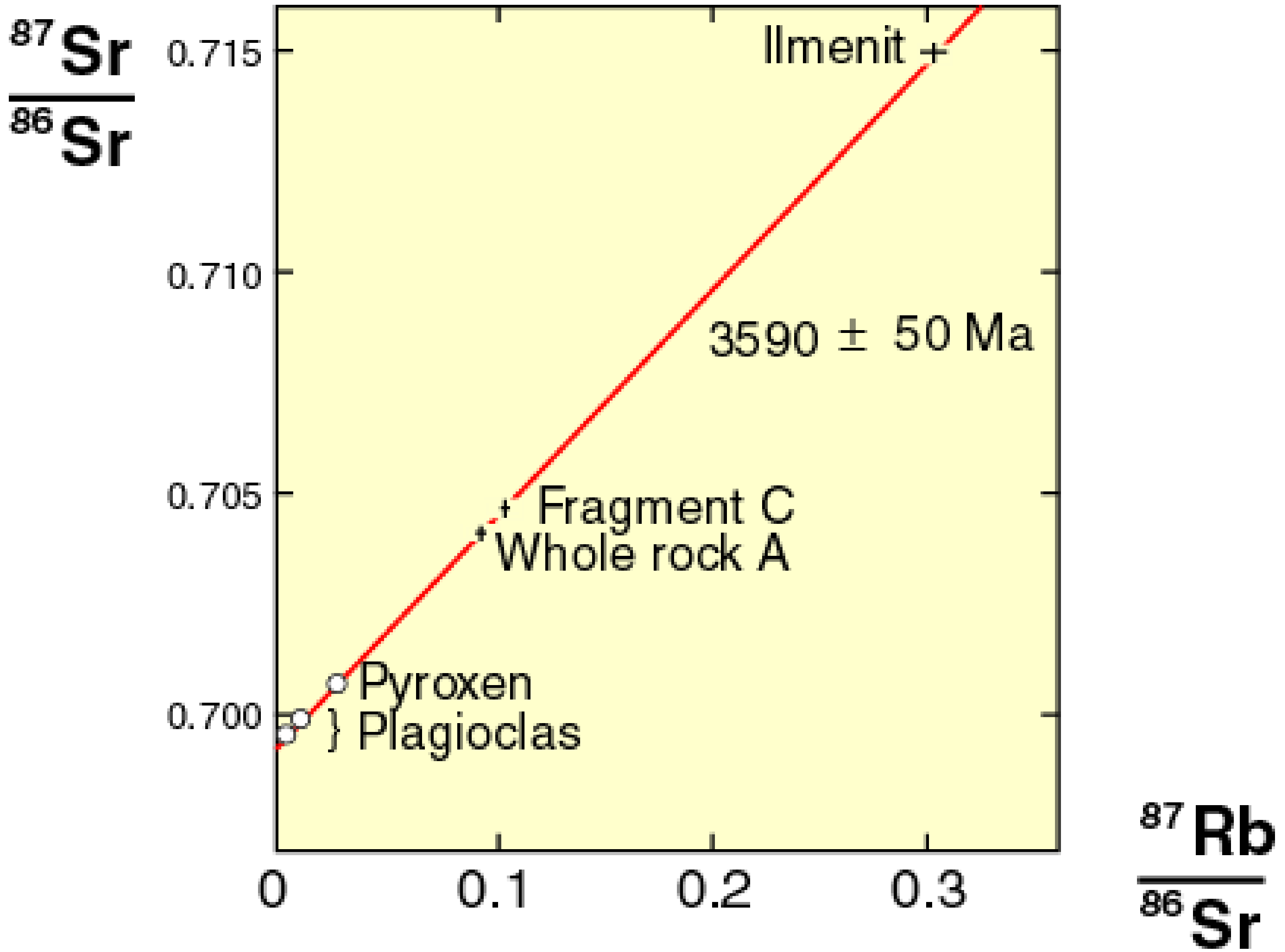


Rb -Sr isochron diagram for whole-rock samples of basaltic achondrites



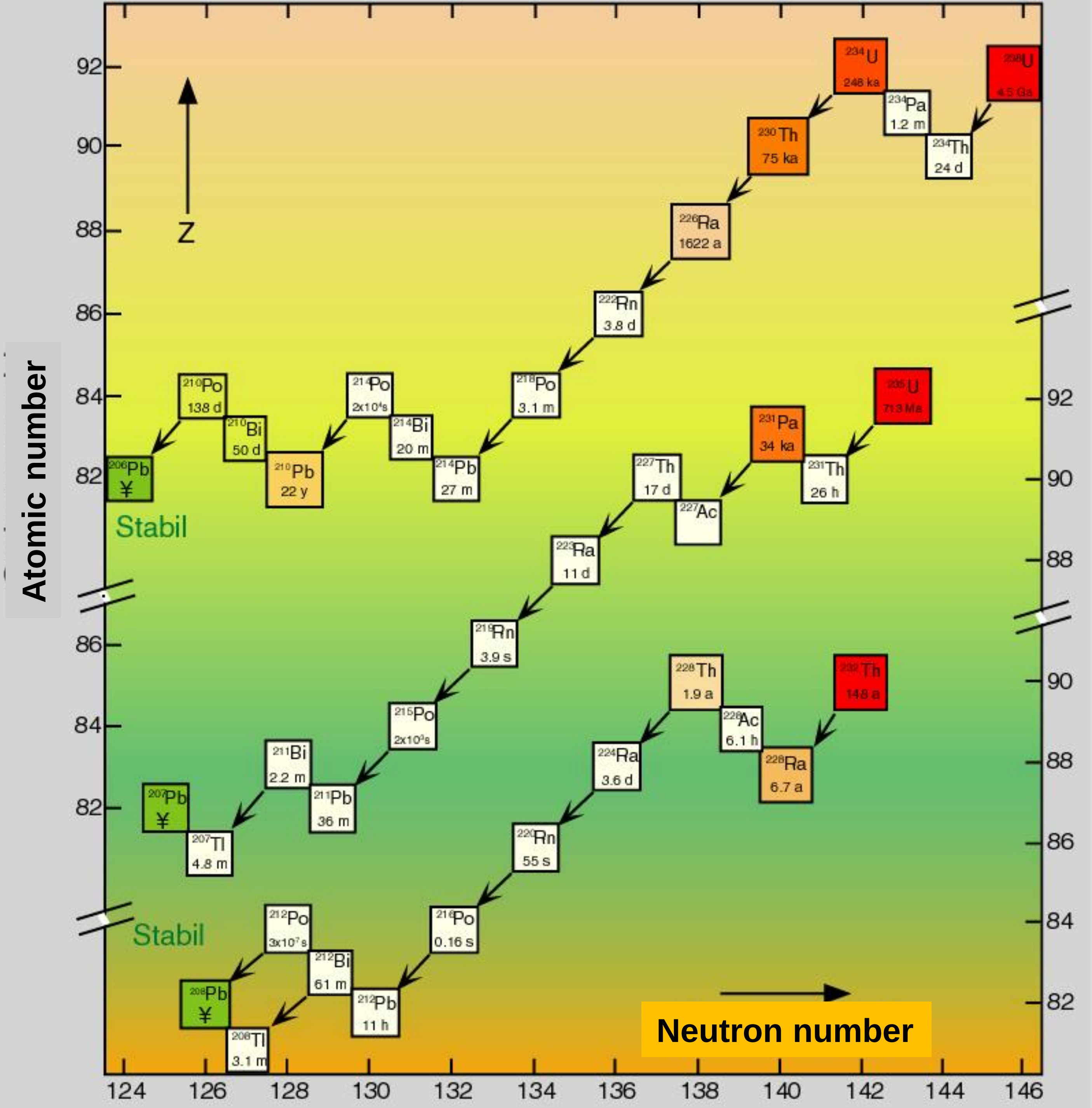
(after Papanastassiou and Wasserburg, 1969)

Rb - Sr einer Mond-Probe 100-17

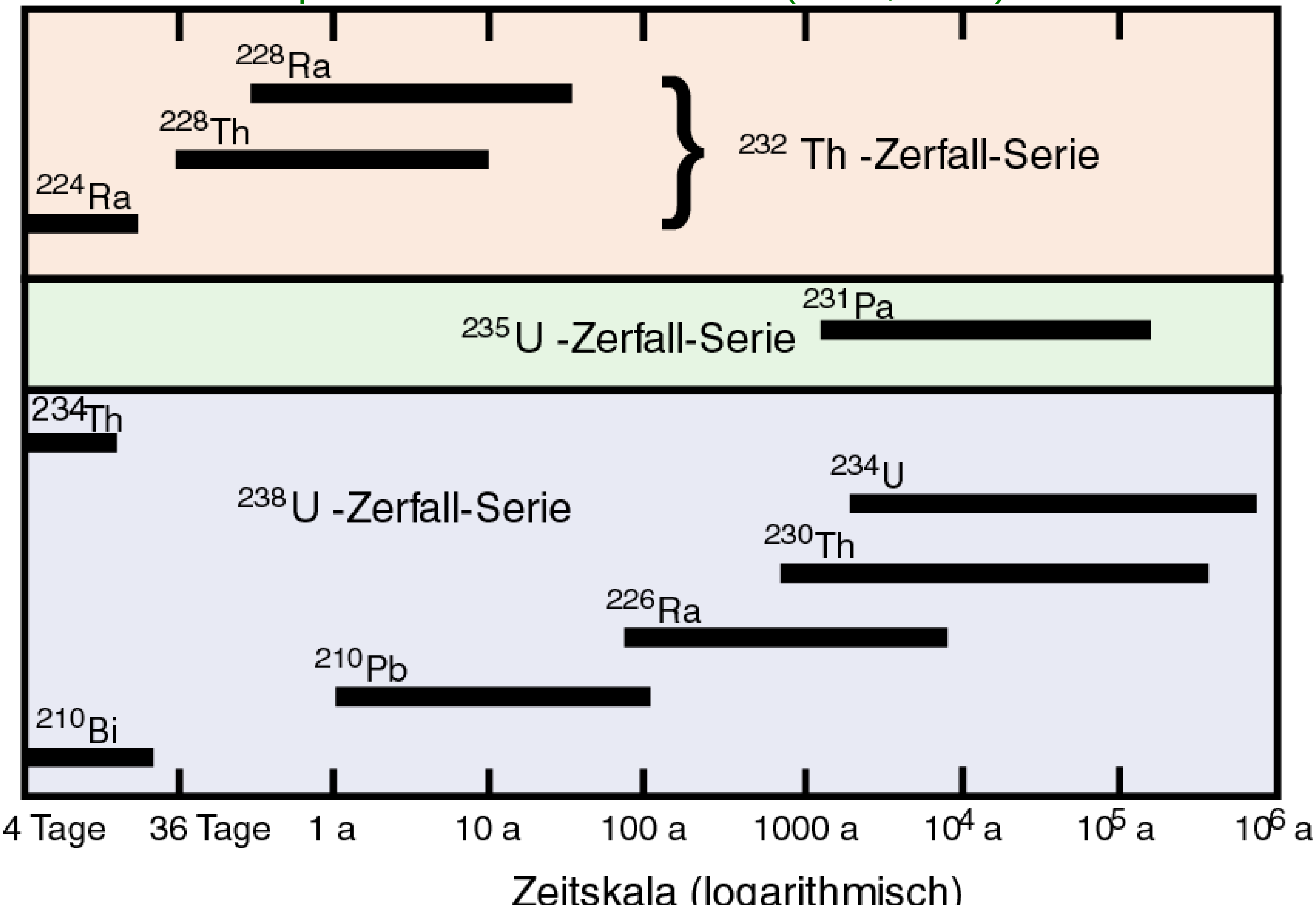


Radioactive decay products of the uranium series (with half-live times) until the final lead isotopes.

➔ This can be used for age determinations of carbonate, bones, teeths volcanic rocks, and sulfides, e.g. $^{230}Th/^{234}U$ (10 ka – 550 ka)



Range of different age deterimations based on decay products of uranium series (Potts, 1987)



Th-U age determination method

- ➔ Uranium is much easyer disolved in watern than thorium
- ➔ This offers two alternative age determination methods (Bender 1985):

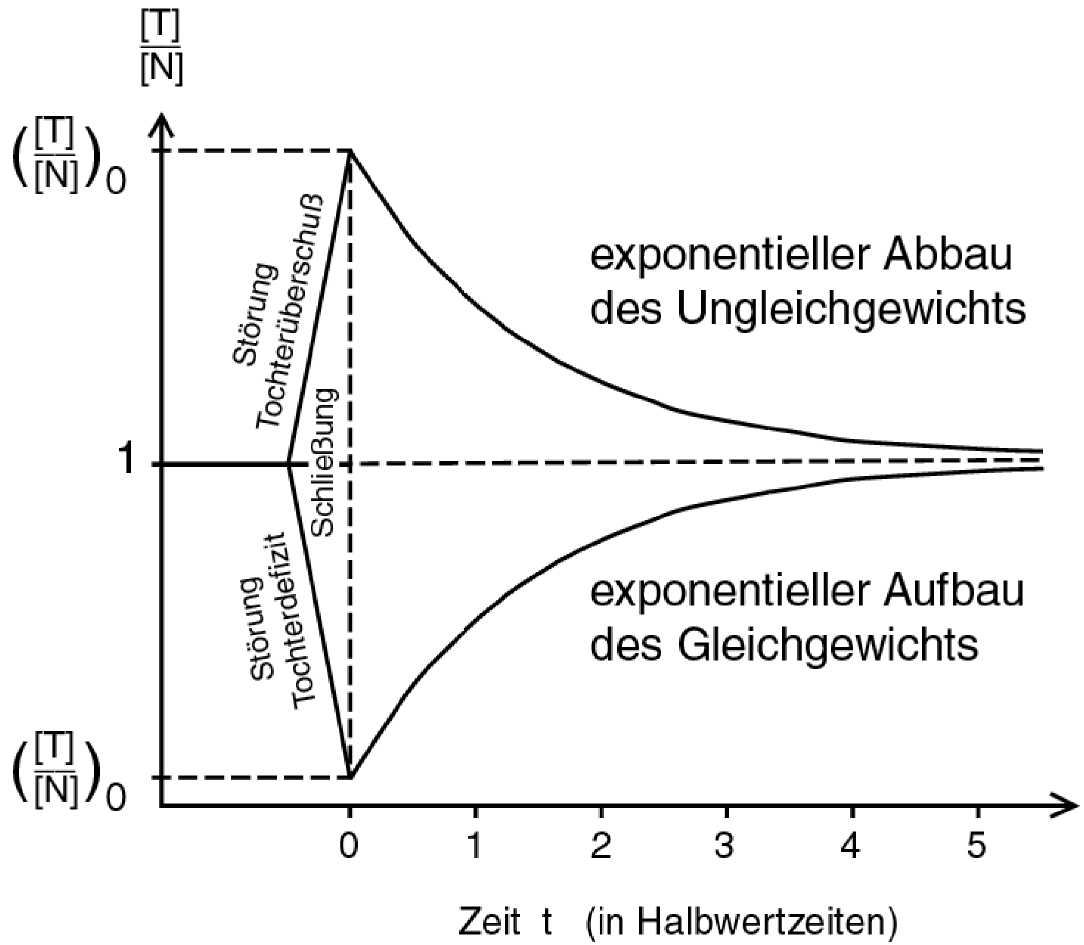
a) Schell, coralls, foraminifera and carbonates built in some uranium in the calicite or aragonite. When this co mponents became isolated from the sea water, the excess ^{234}U starts to decay to ^{230}Th until a secondary equilibrium between both isotopes. Considering that the activity of ^{230}Th is cero in freshly formed $CaCO_3$ than the decrease in this disequilibrium can be used as trace for the age.

b) Due to the fast sedimentation of Thorium from the marine water many young pelagic sediments are characterised by a thorium excess. This disequilibrium tends to form a new equilibrium with the ^{234}U content .

N = radiogenic
mouther nuclide

T = radiogenic
daughter nuclide

Disturbances of theT/N ratio
Can be caused by various
chemical, physical and
biological processes.



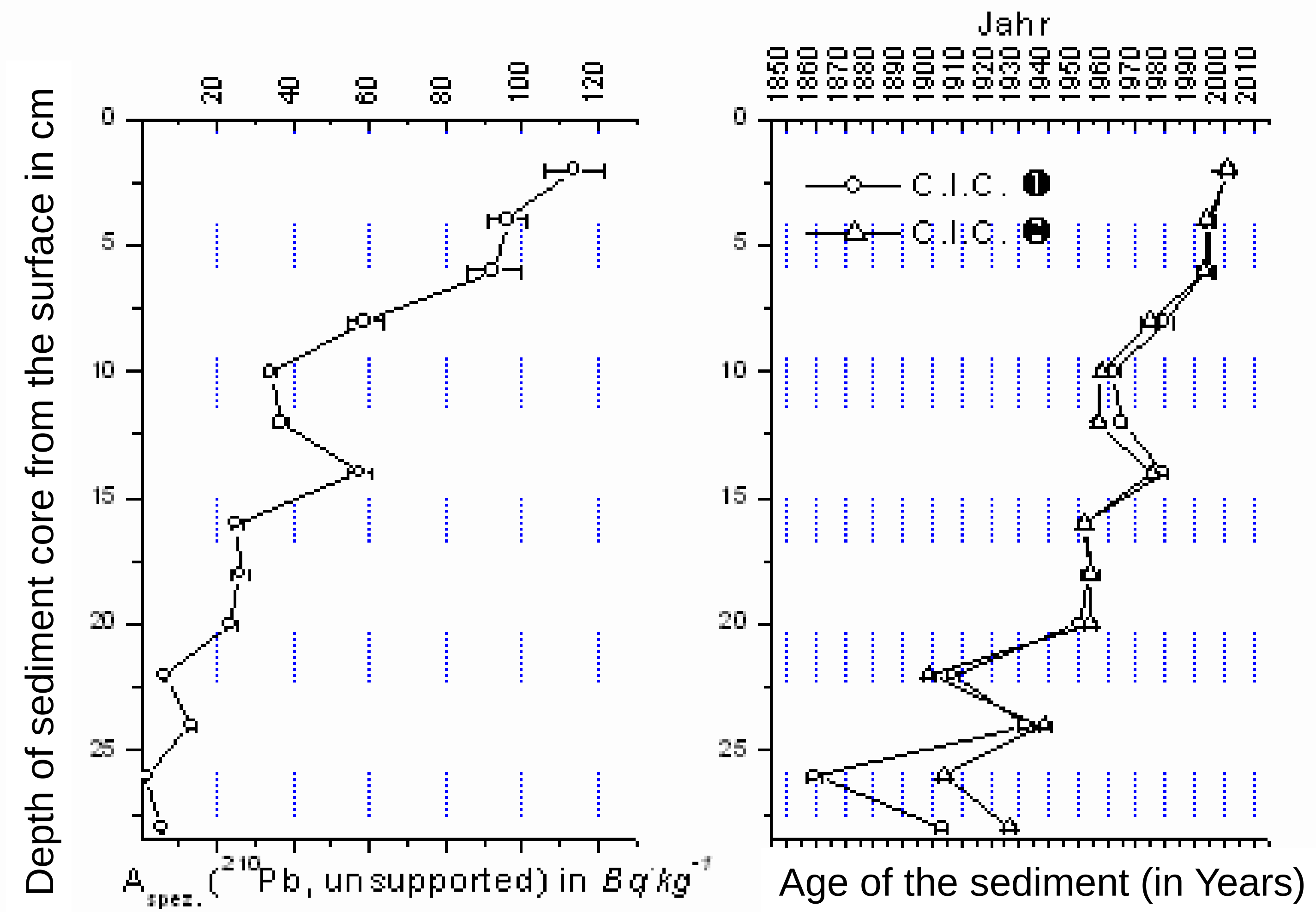
^{210}Pb ages: Time window of the last 150 years

Dating of superficial secitions of:
➔ice cores (*H. Gäggler*)
➔sediments (*C. Schelske*)
➔peat (*F. El-Daoushy*)

Based on the auf Eintrag von atmospheric unsupported ^{210}Pb,

⇒ It is measured by gammaspectrometry using the 46,5 keV gamma line (P_γ = 0,0424)
⇒ Due to the natural ^{226}Ra content of all sediments and additional amount of supported ^{210}Pb must be considered and corrected

^{210}Pb sediment ages



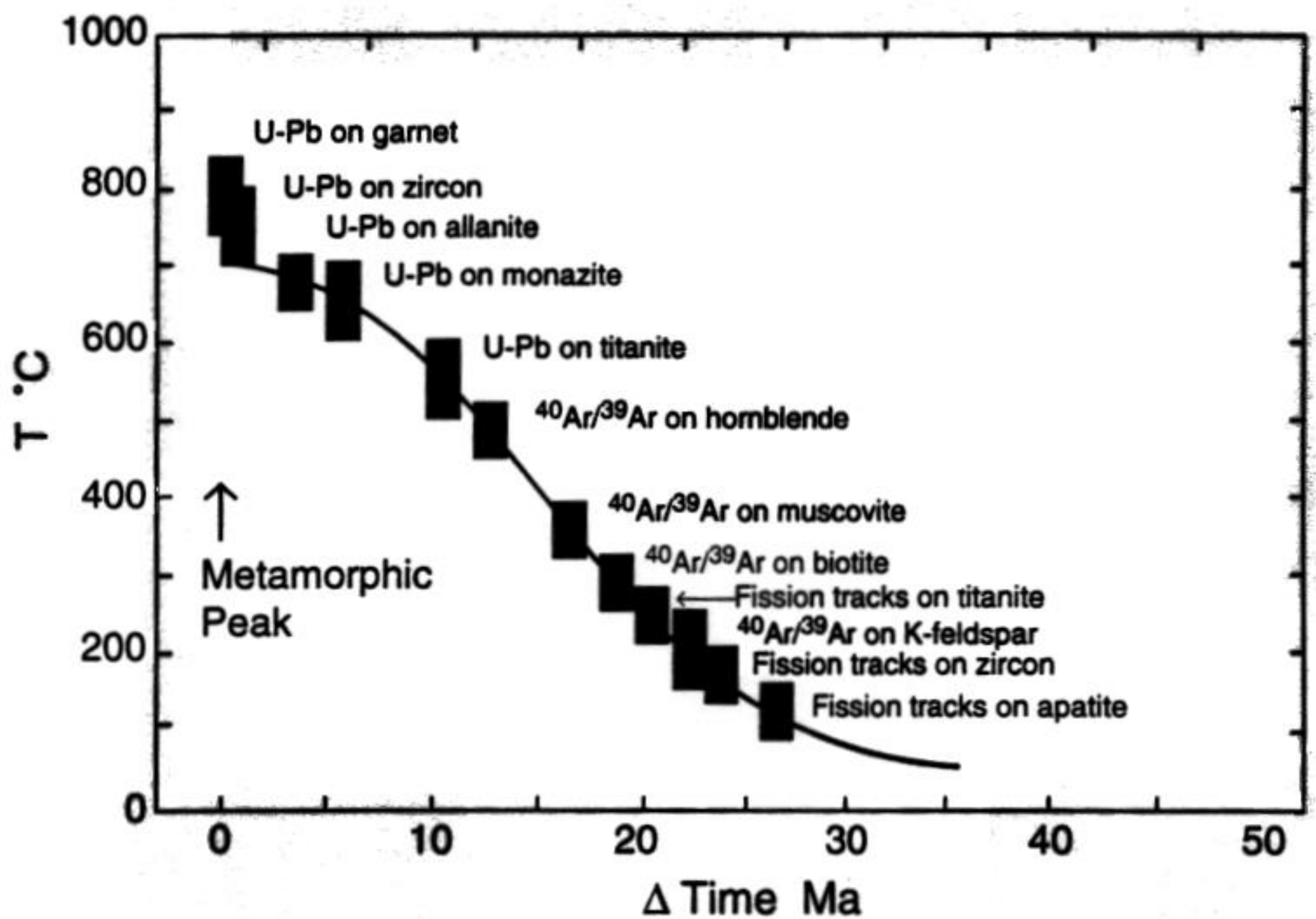
Specific activities from Azap-See sediments for ^{210}Pb (unsupported) plotted against core depth and calculatzed sediment ages (right) (C.I.C.-Model; S. Ritzel).

Annual cyles:

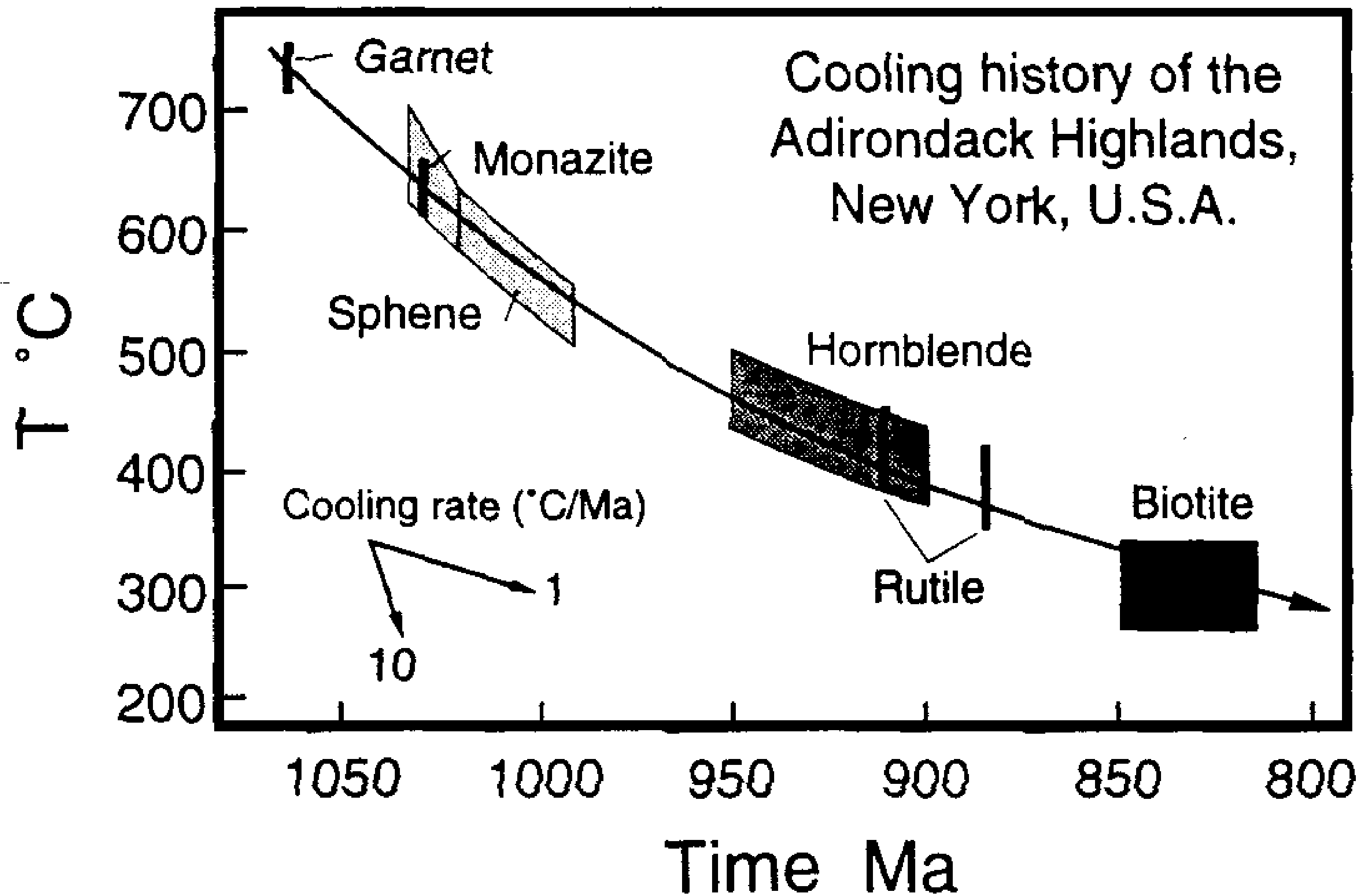
Warve chronologies:	Annual cycles in the sediment composition of the deposited sediments
Tree rings:	Annual changes of the cell structure of the newly form wood rings
Annual firn and ice layers	Ice and firn layers: Seasonal changes of th chemical and isotopic characteristics of the snow

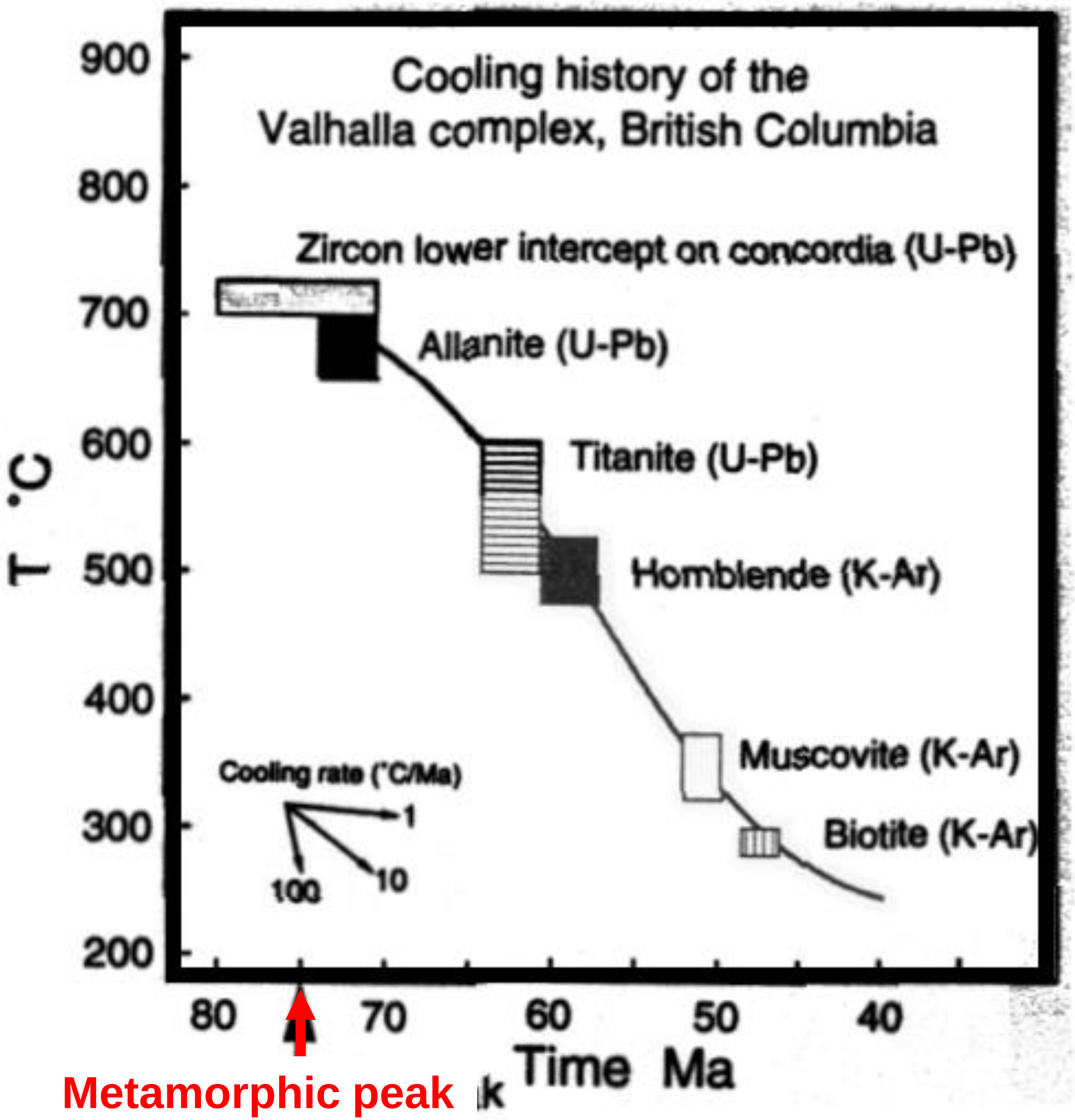
7.3.3.7 Cooling history of rocks

The temperature-time path shown below is derived from different dating methods which indicate ages since the rock fall below a certain temperature (closure of the system)



Cooling histrory of Adirondack Highlands, New York. U-Pb of garnet, monazite, rutile and sphen as well a Ar-Ar ages of amphibole and biotite





Temperature-time-path for the cooling of the Valhalla complex. Cooling rate
➔ 10°C/Ma.

Cooling history based on mineral ages with different closing temperatures of the syenite (a plutonic rock) of Glen Dessary in Scotland