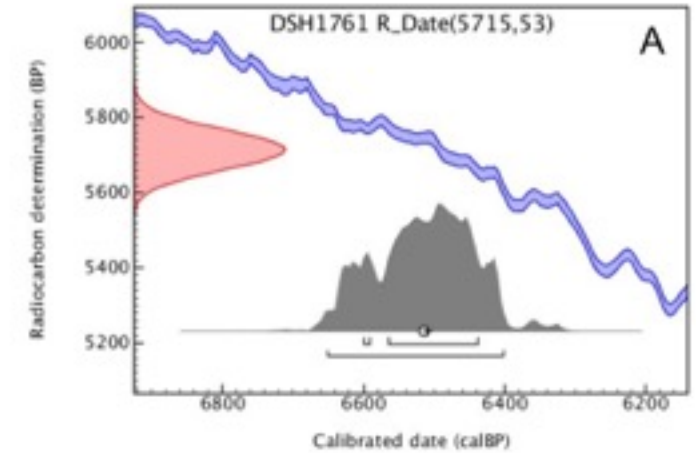
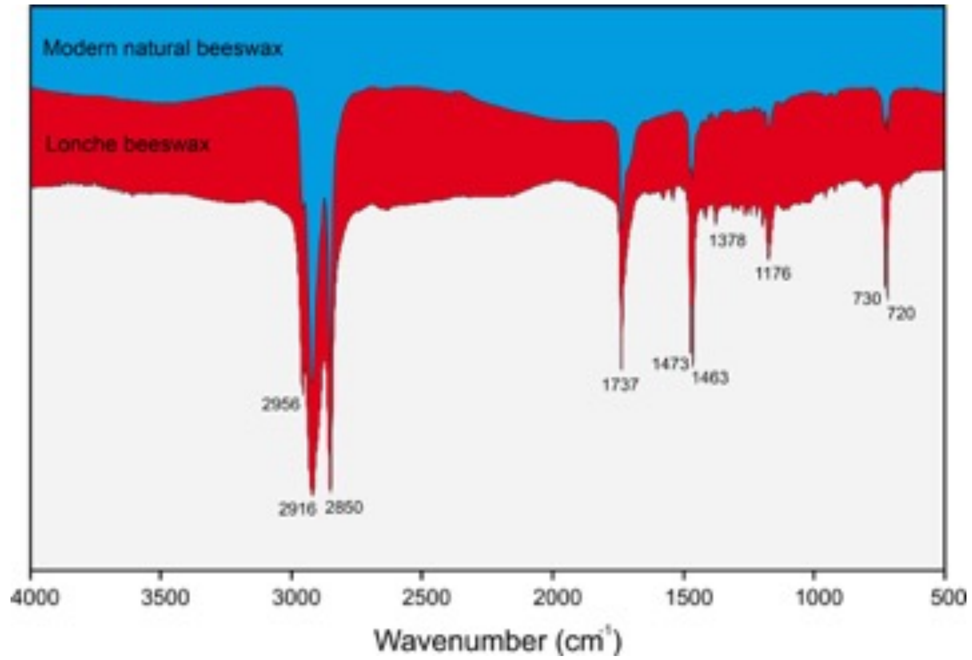
OPEN ACCESS Freely available online

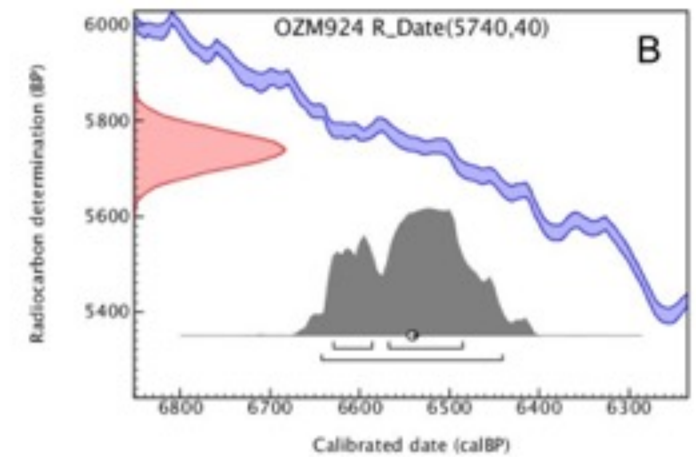
PLOS ONE

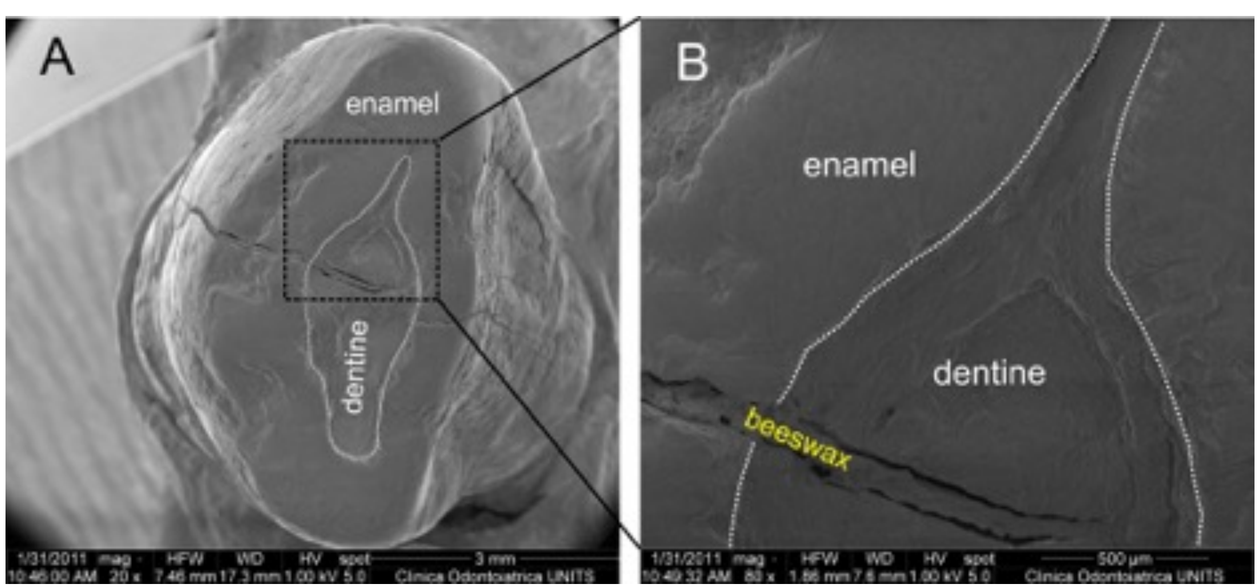
Beeswax as Dental Filling on a Neolithic Human Tooth

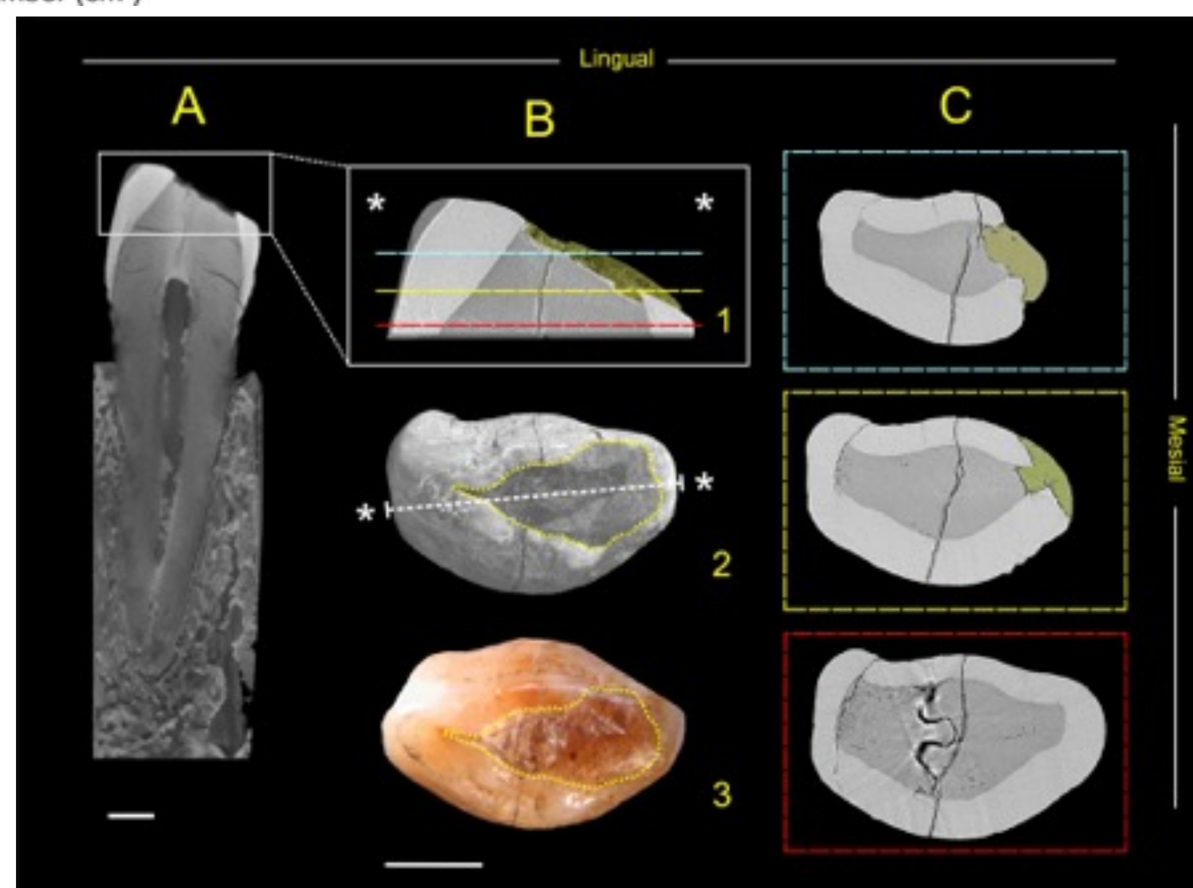
Federico Bernardini[1]*, Claudio Tuniz[1,2], Alfredo Coppa[3], Lucia Mancini[4], Diego Dreossi[4], Diane Eichert[4], Gianluca Turco[5], Matteo Biasotto[5], Filippo Terrasi[6], Nicola De Cesare[7], Quan Hua[8], Vladimir Levchenko[8]











ARCHMAT
Advanced Analytical Methods

Claudio Tuniz

Introduction

Dating methods

- Radiocarbon (^{14}C)
- Radioberyllium ($^{10}Be/^{9}Be$)
- In-situ cosmogenic isotopes (^{10}Be, ^{26}Al)
- Potassium-Argon (^{40}K-^{40}Ar)
- Uranium-series
- Luminescence (TL, OSL, ESR)
- Fission track dating
- Amino Acid Racemization
- Archeomagnetism dating

Microanalytical methods

- X-ray microtomography
- Ion beam analysis
- Neutron tomography
- X-ray microfluorescence
- x-ray diffraction
- Laser Ablation Inductively Coupled Plasma Mass Spectrometry

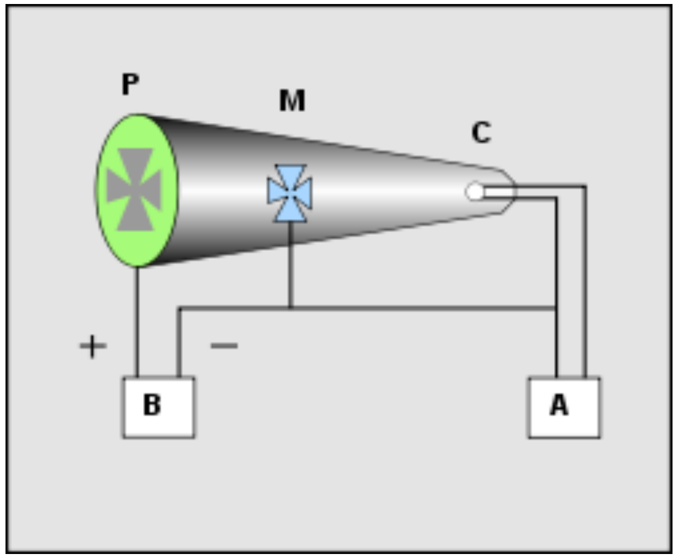
Exploration

- Satellite
- Geo-radar
- Laser scanning

Introduction

Radiation

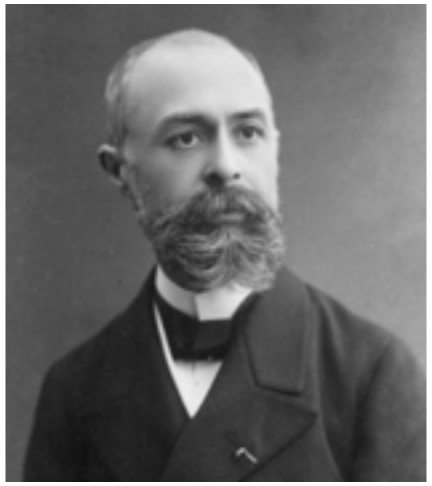
- Cathode rays
  - Discovered J. Hittorf 1869
  - Kathodestrahlen E. Goldstein,1876
  - ‘Corpuscles’ 1897 (J.J. Thompson), negatively charged, ~1800 times lighter than hydrogen atom
  - **Electrons**

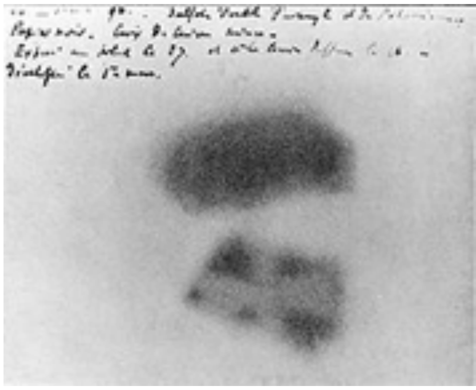


Radiation

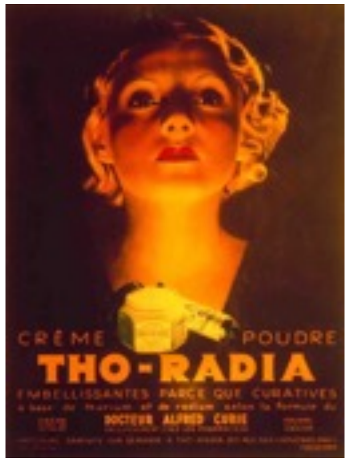
✤ X-rays W C Roentgen 1895

✤ 'Uranium rays' H Becquerel 1896



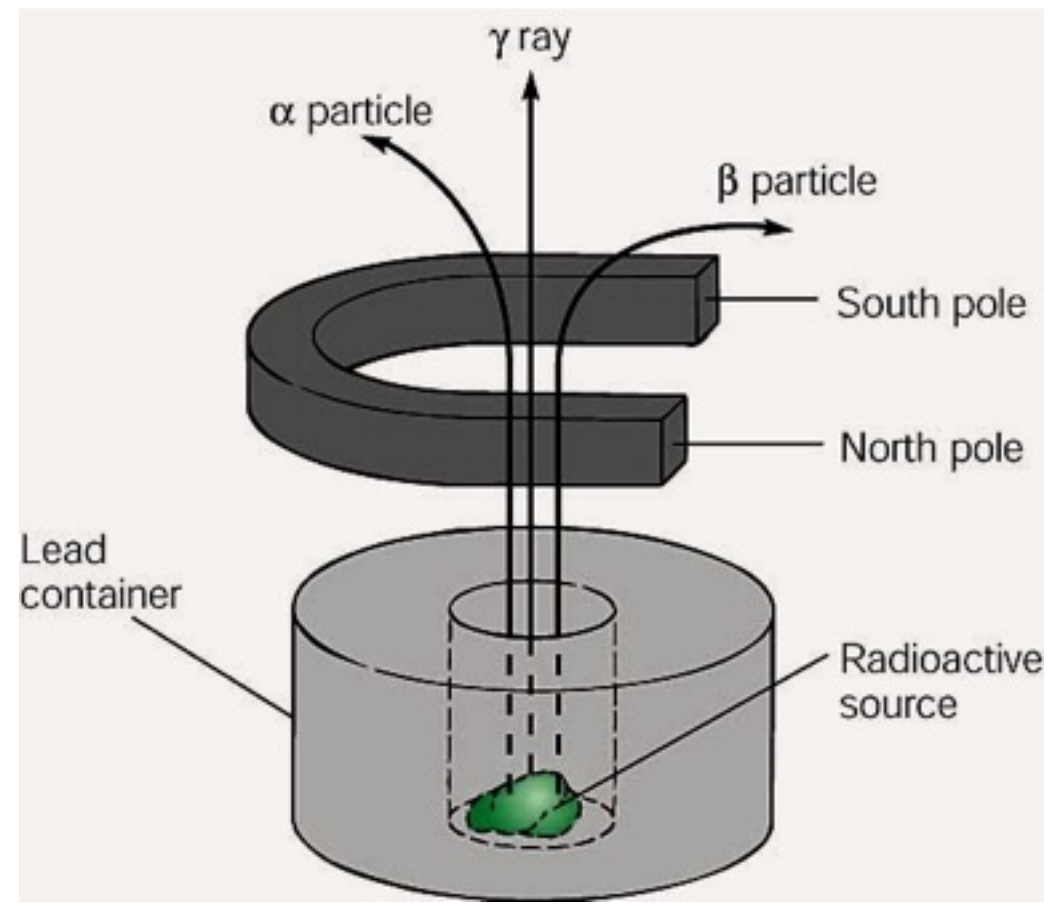


✤ 'Radioactivity' P & M Curie 1898



Radiation

Radiation passing through a magnetic field shows that massive, positively charged alpha particles are deflected one way, and less massive beta particles with their negative charge are greatly deflected in the opposite direction. Gamma rays, like light, are not deflected.



Basic equations of mass spectrometry

$$\frac{1}{2}mv^2 = zV$$

Ion's kinetic E function of accelerating voltage (V) and charge (z).

$$F = mv^2 / R$$

Centrifugal force

$$F = Bzv$$

$$mv^2 / R = Bzv$$

Balance

Combine equations to obtain:

$$m / z = B^2 R^2 / 2V$$

Fundamental equation of mass spectrometry

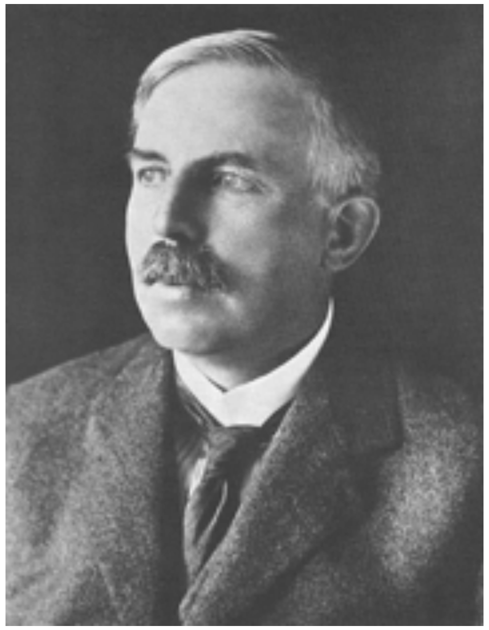
Change 'mass-to-charge' (m/z) ratio by changing V or changing B.

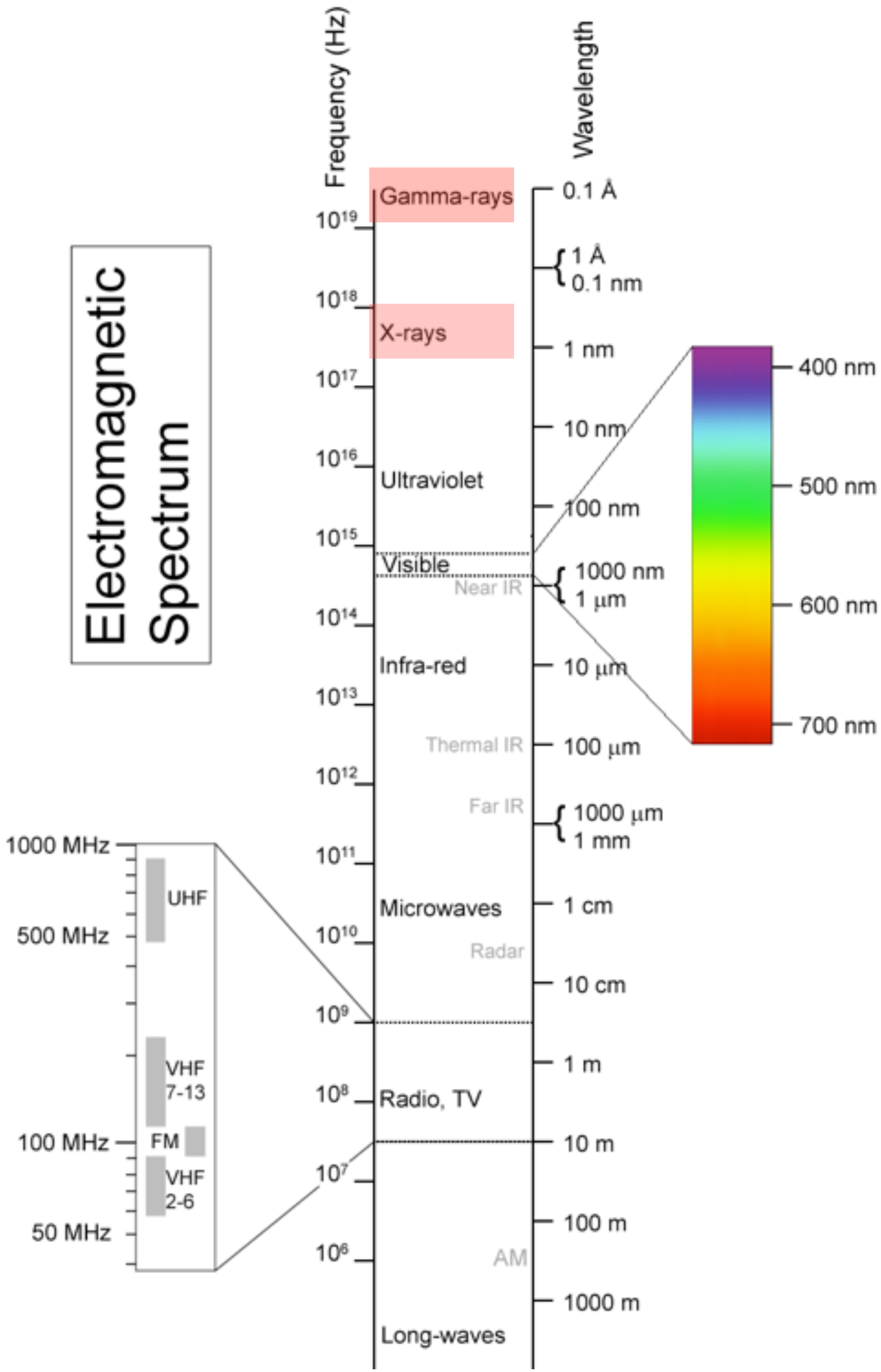
NOTE: if B, V, z constant, then:

$$R \propto \sqrt{m}$$

Radiation

- beta particles **(β)** Rutherford 1898
- alpha particles **(α)** " "
- gamma rays **(γ)** Villard 1900



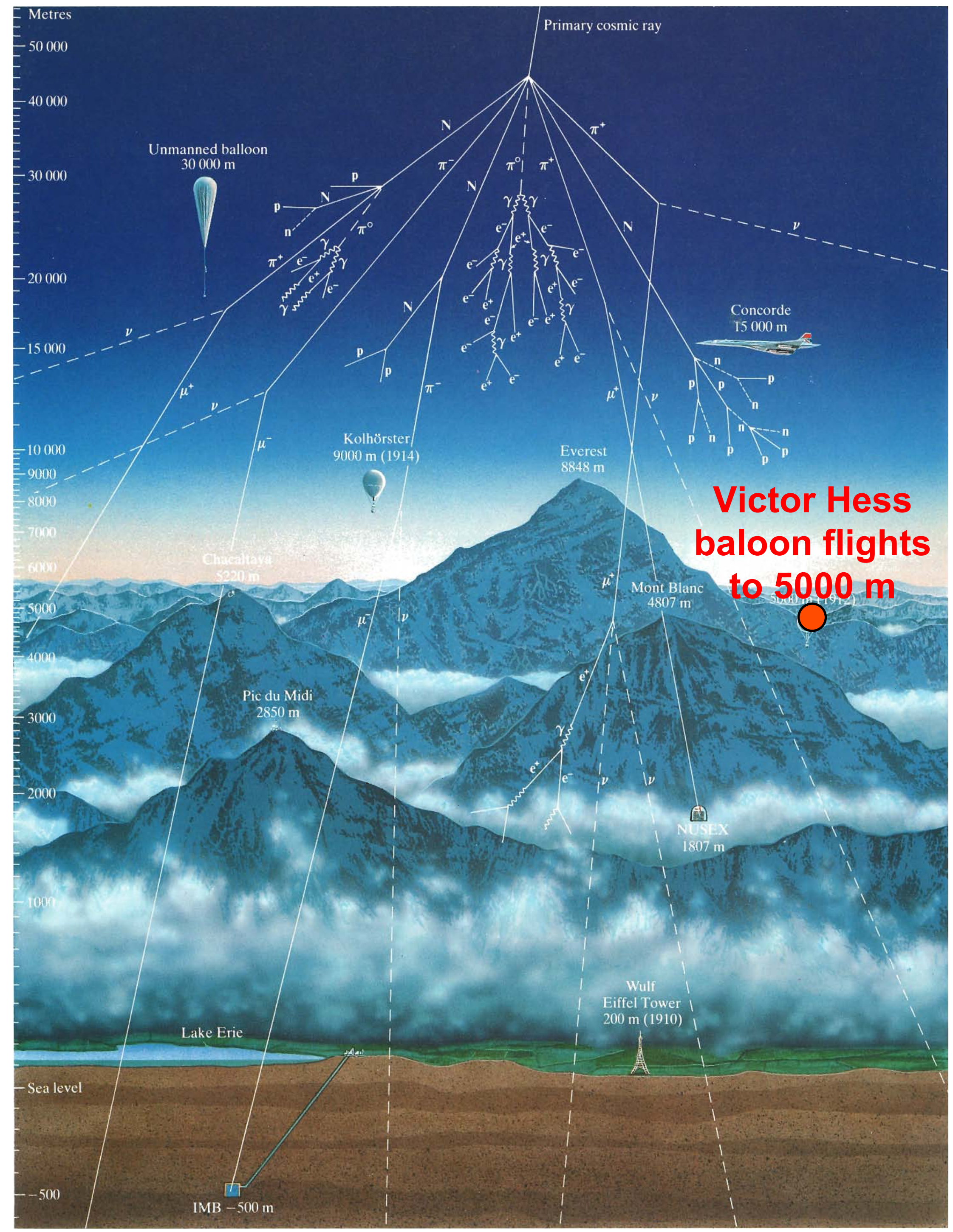


Electromagnetic Spectrum
Frequency (Hz)
Wavelength
Gamma-rays
X-rays
Ultraviolet
Visible
Near IR
Infra-red
Thermal IR
Far IR
Microwaves
Radar
Radio, TV
AM
Long-waves
10^{19}
10^{18}
10^{17}
10^{16}
10^{15}
10^{14}
10^{13}
10^{12}
10^{11}
10^{10}
10^{9}
10^{8}
10^{7}
10^{6}
0.1 Å
1 Å
0.1 nm
1 nm
10 nm
100 nm
1000 nm
1 µm
10 µm
100 µm
1000 µm
1 mm
1 cm
10 cm
1 m
10 m
100 m
1000 m
400 nm
500 nm
600 nm
700 nm
1000 MHz
500 MHz
100 MHz
50 MHz
UHF
VHF
7-13
FM
VHF
2-6

Radiation

- neutrons J. Chadwick (1932)
- positrons C. Anderson (1932)
- muons J C Street & E C Stevenson (1937)

Victor Hess, 1912



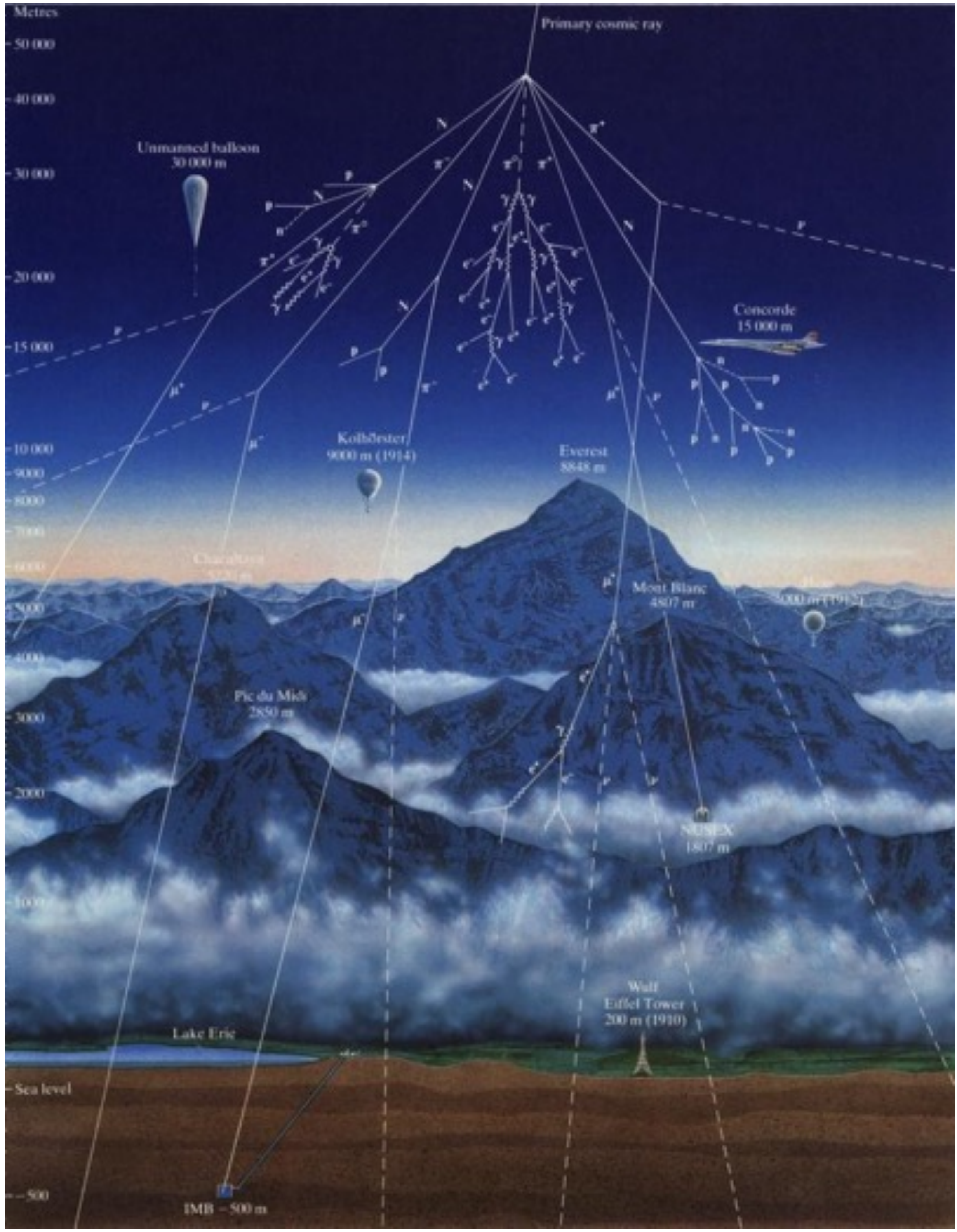
Natural Radioactivity & Ionising Radiation

Radioactivity: Atomic nuclei spontaneously emit ionising radiation

Ionising radiation: Particles or electromagnetic waves that can deposit energy creating free electrons and ions

Origin: terrestrial (U, Th, K-40, cosmogenic) and extraterrestrial (solar, galactic)

Every second, at least one muon, a particle like an electron but about 200 times heavier, crosses your body.



http://www.atral.com/U238.html

Radioactive decay

(Rutherford, Soddy, 1908)

$$N(t) = N_o e^{-\lambda t}$$

$N(t)$, number of radionuclides at time t

N_o, number of radionuclides at t=0

λ, decay constant.

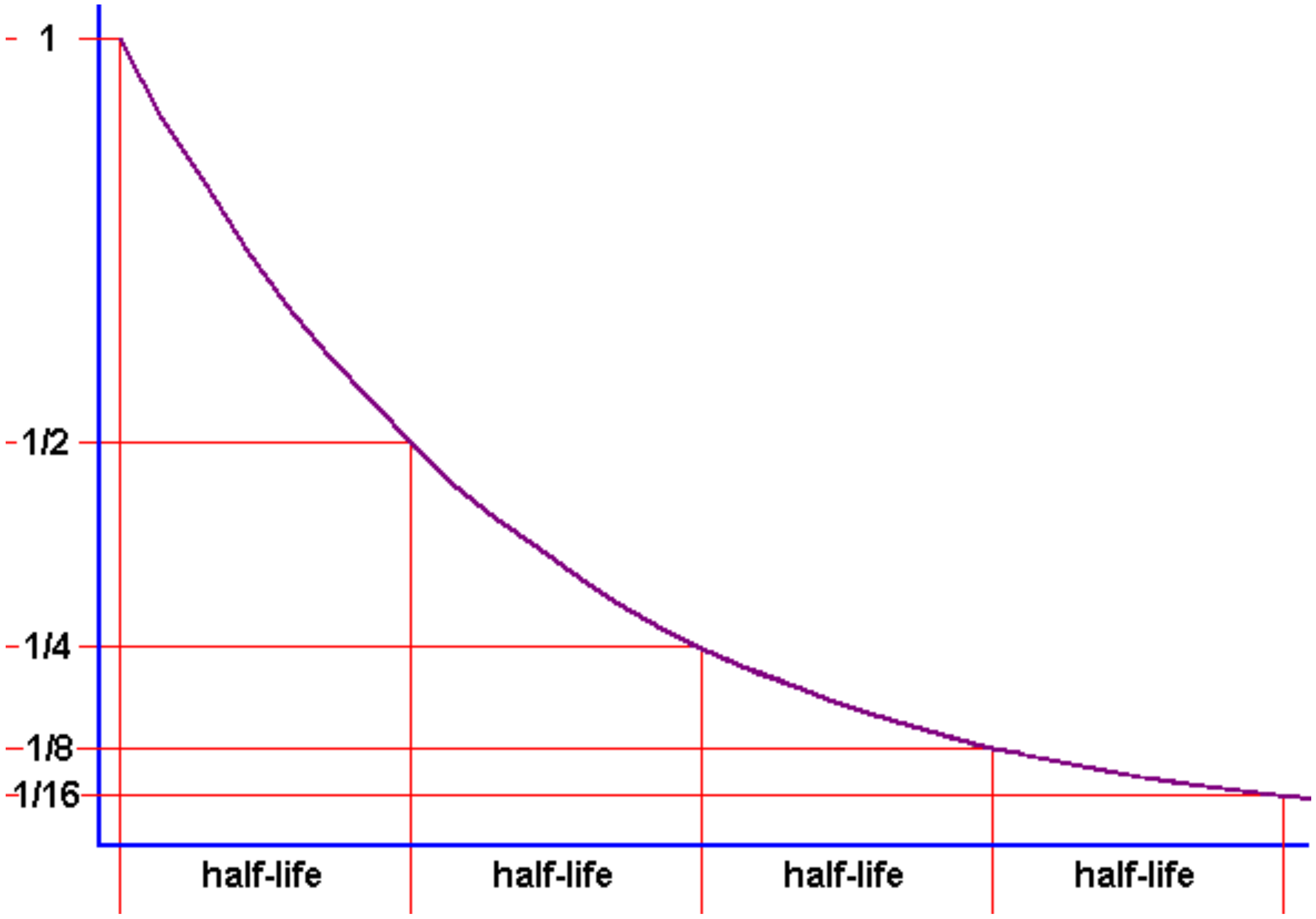
The decay constant λ is related to the half life $t_{1/2}$ by:

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

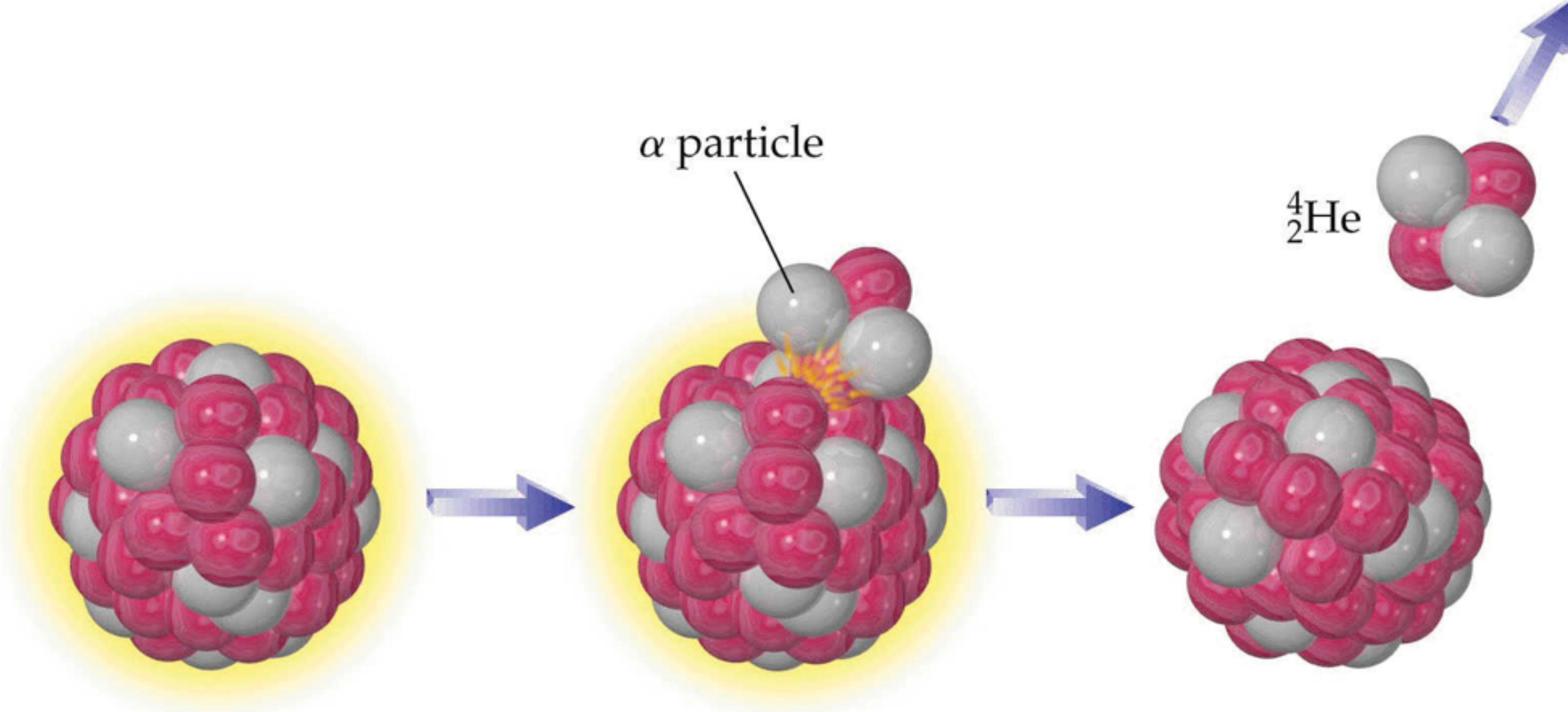
Determining Half Life

- $N = N_0 \exp(-\lambda t)$
- Solve for $N = N_0/2$
- $N_0/2 = N_0 \exp(-\lambda\ t_{1/2})$
- $½ = \exp(-\lambda\ t_{1/2})$
- $-\mathrm{Ln}(2) = -\lambda\ t_{1/2}$
- $t_{1/2} = \mathrm{Ln}(2)/\lambda = 0.693/\lambda$

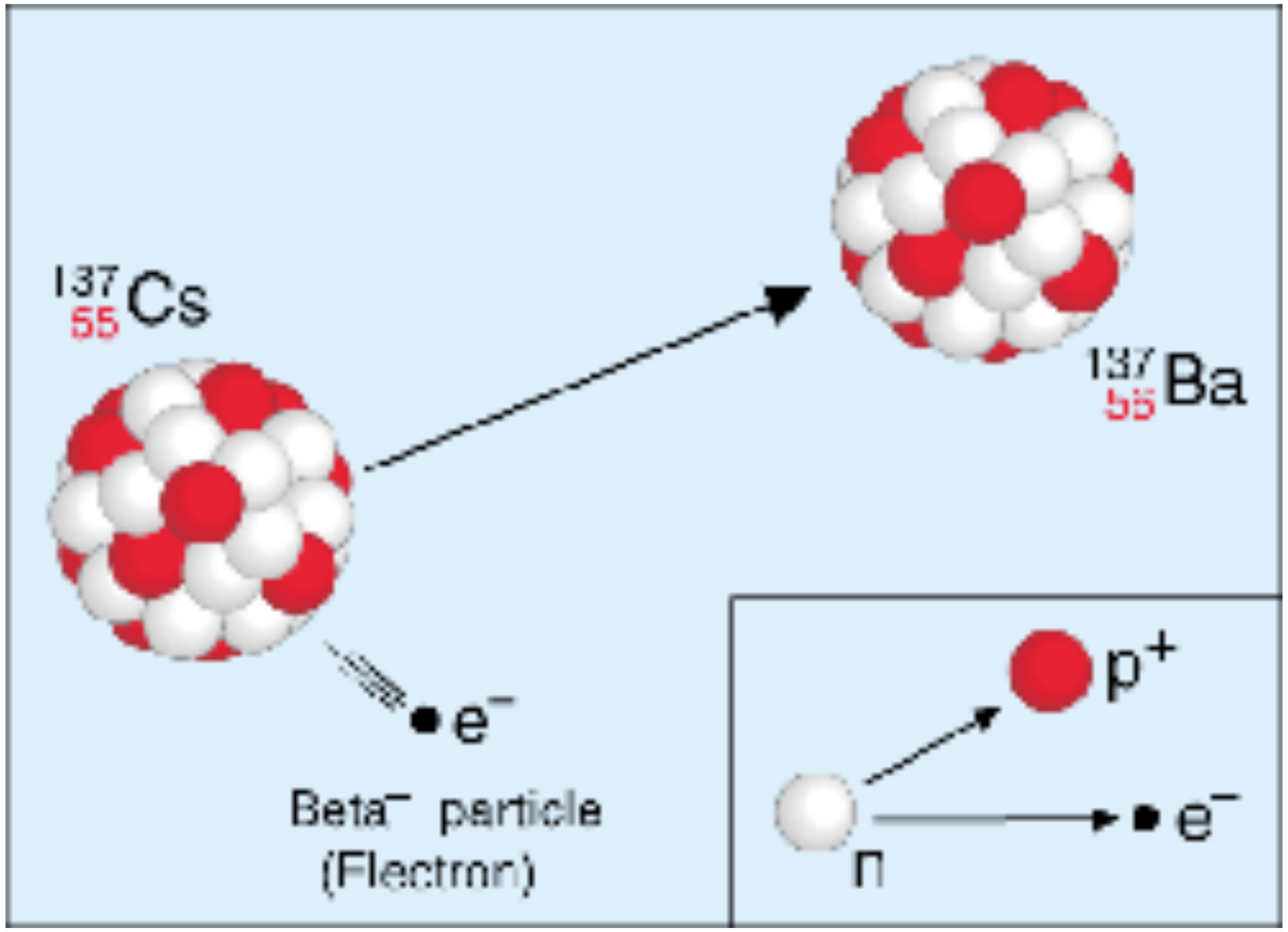
Half-Life



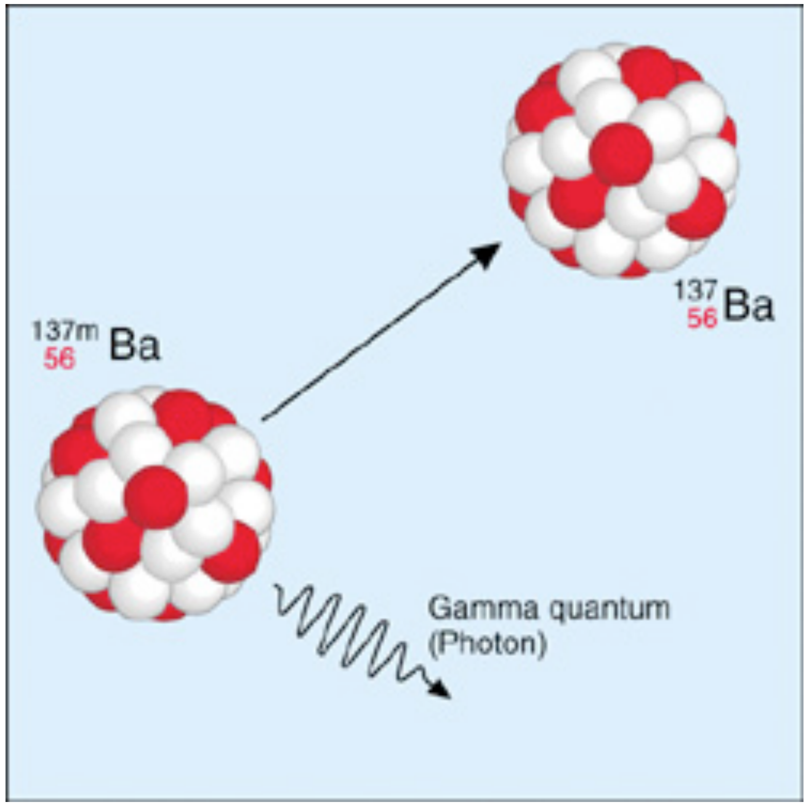
alpha radioactivity



beta radioactivity



gamma radioactivity



Nuclear reactions

(Rutherford 1919)

$$ {}^{4}_{2}He_{2} + {}^{14}_{7}N_{7} \longrightarrow {}^{17}_{8}O_{9} + {}^{1}_{1}H_{0} $$

Dating methods

Radiometric dating

- 1905: Rutherford first to use U to measure age using helium accumulated in U-rich minerals; he obtains an age of 500 ka (but helium leaks ...only minimum age
- Boltwood measured lead in uranium minerals
- 1911: Arthur Holmes obtaines first U-Pb age of 370 Ma in rock from Norway
- Almost all dating now involves use of mass spectrometers (developed in 1940's)

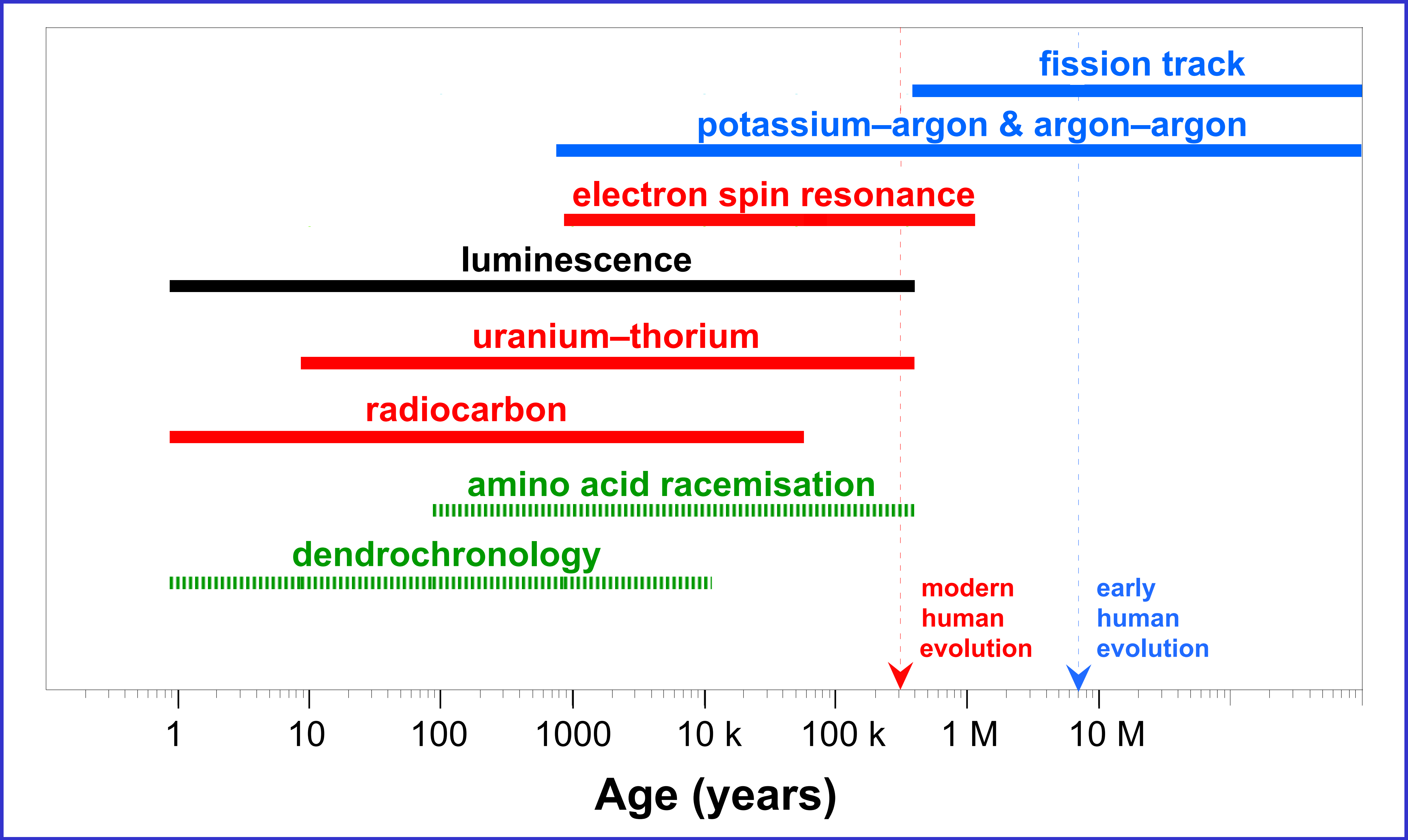
Radioactive nuclide methods

- Radioactive decay, e.g. Radiocarbon dating
- Ingrowth radionuclide, e.g. Potassium-argon

Radiative dosimetry methods

- TL
- OSL
- ESR
- Fission track

Dating methods



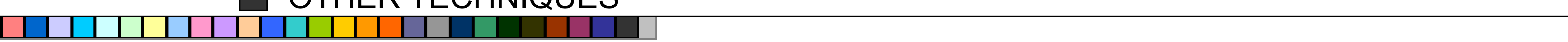
Dating materials

Method \ Material	Wood/ Plants	Bones	Tooth Enamel	Shells	Egg Shells	Corals	Speleo-thems	Sediments	Surfaces	Obsidian Glass	Volcanic Minerals	Burnt Flint	Pottery
Dendrochronology	yellow												
Radiocarbon	yellow	green	green	yellow	yellow	yellow	yellow	red					green
K/Ar & Ar/Ar											yellow		
U-series	green	green	red	red	yellow	yellow	yellow	green			yellow		
Fission Tracks										yellow	yellow		
Luminescence							green	yellow		green	green	yellow	yellow
ESR			yellow	green	red	green	green				green	green	
Amino Acid		red	red	green	yellow								
Hydration										yellow			
Cosmogenic Isotopes								yellow	yellow				

(yellow) well suited materials (green) results may sometimes be unreliable (red) results often unreliable

Microanalytical methods

- OPTICAL MICROSCOPY
- PHOTOGRAPHY
- ELECTRON MICROSCOPY
- INFRARED SPECTROMETRY
- X-RAY DIFFRACTOMETRY
- CHROMATOGRAPHY
- COLORIMETRY
- RADIOGRAPHY
- X-RAY FLUORESCENCE ANALYSIS
- ENVIRONMENTAL WEATHERING
- VISIBLE ULTRAVIOLET SPECTROMETRY
- DIGITISATION OF IMAGES
- COMBINED CHROMATOGRAPHY / MASS SPECTROMETRY
- MASS SPECTROMETRY
- THERMAL ANALYSIS
- MECHANICAL TESTING
- MATERIALS
- RAMAN SPECTROMETRY
- ATOMIC EMISSION SPECTROSCOPY
- DATING TECHNIQUES
- ATOMIC ABSORPTION SPECTROSCOPY
- NON-DESTRUCTIVE TESTING
- ION BEAM ANALYSIS
- SURFACE ANALYSIS TECHNIQUES
- SYNCHROTRON RADIATION EXAMINATION
- ATOMIC FORCE MICROSCOPY
- MOESSBAUER ANALYSIS
- ACTIVATION ANALYSIS
- MICROBIOLOGICAL ANALYSIS
- NUCLEAR MAGNETIC RESONANCE ANALYSIS OR IMAGING
- PHOTOGRAMMETRY
- OTHER TECHNIQUES



Relative frequency of use of techniques