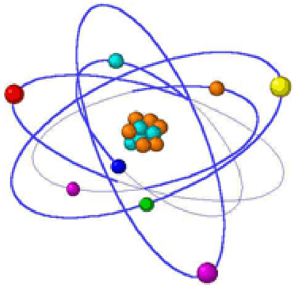
Radiation Biology, Protection and Applications (FS2018)



Applications in Natural Sciences: Neutron Activation Analysis, Nuclear Dating (Week 14, seminar)

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Neutron Activation Analysis (NAA), Nuclear Dating (ND): Outline

Lecture 1 (NAA)

- ❑ Introduction
- ❑ Basics: Principle of NAA
- ❑ Detection Limits
- ❑ Techniques and Sources
- ❑ Variations of NAA
- ❑ Examples
  - Main Fields of NAA-Applications
  - Detection of Bromine in Food
- ❑ Activation by Charged Particles
- ❑ Activation by Photons

Lecture 2 (ND)

- ❑ Introduction
- ❑ Basics: Decay and Equilibria
- ❑ Nuclear Dating: Overview
- ❑ Terrestrial Mother/Daughter Pairs
- ❑ Natural Decay Series
- ❑ Cosmogenic Radionuclides
- ❑ Radiocarbon Dating:
  - Basics
  - Calibration
  - Measurement (AMS)
  - Examples

❑ Summary

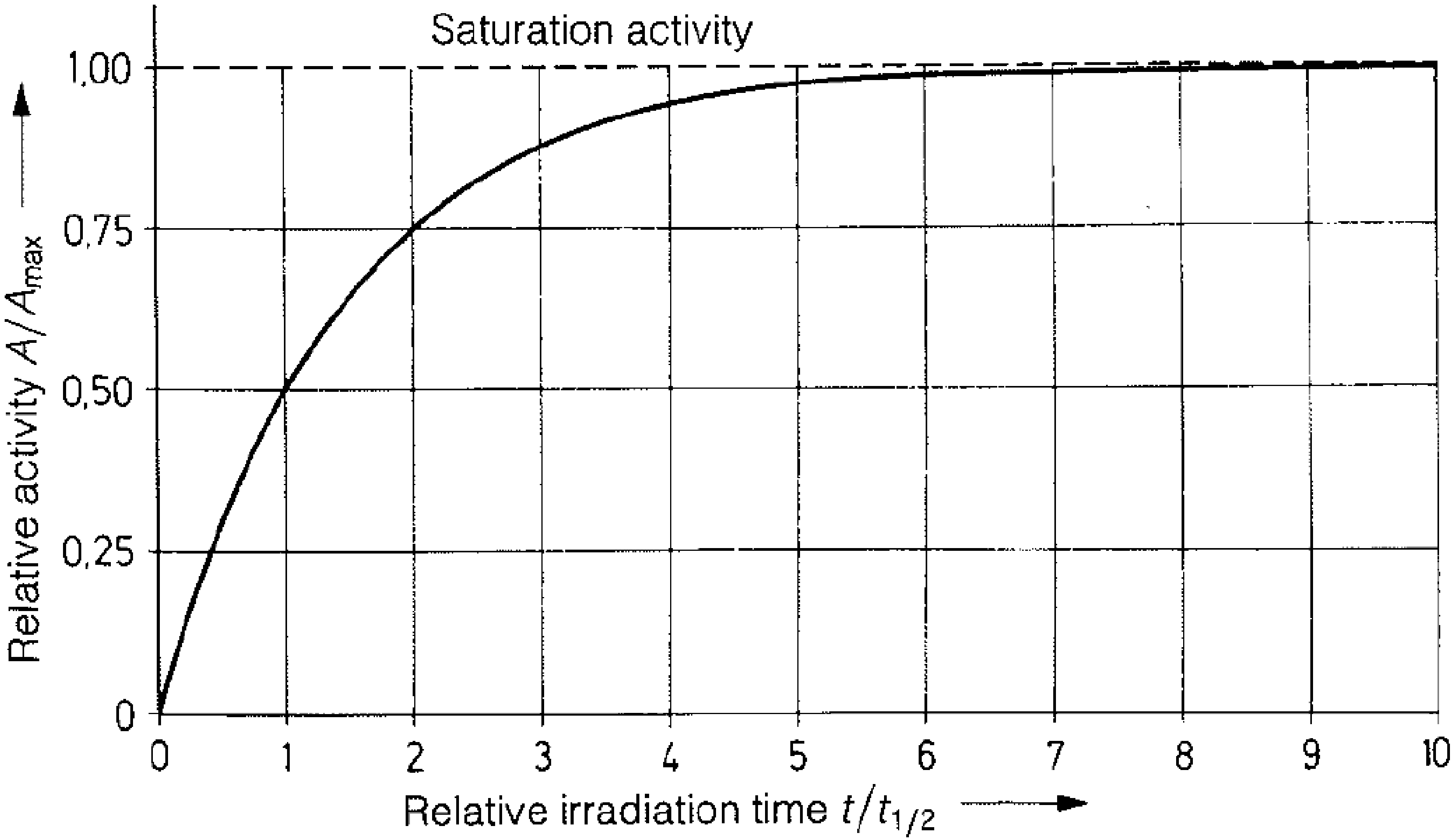
Introduction

- ☐ NAA is a method to determine the concentration of elements in a wide variety of samples, i.e., a vast amount of materials.
- ☐ The **advantages of NAA** are:
  - It does not destroy the sample (**non-destructive analysis**) and therefore:
    - can be used to analyze works of art or historical artifacts
    - is not subject to sample preparation or after-treatment (which both may introduce unwanted impurities)
  - It has a very **high sensitivity**, and thus gives **very accurate results**.
  - A large number of trace elements (up to about 70) can be determined simultaneously.
  - It is generally recognized as the **"referee method"** of choice when new procedures are being developed or when other methods yield results that do not agree (**blank-free technique**).
- ☐ Disadvantages of NAA are:
  - The irradiated sample may remain radioactive after analysis and may require handling and disposal as radioactive waste.
  - As the number of suitable activation facilities (especially nuclear reactors) is declining, the technique has become more expensive and has been applied to a lesser extent in recent years.

Yield of Nuclear Reactions

- The **production rate** of nuclide P in the nuclear reaction T + x → P + y is given by (the activation equation): $dN_P/dt = \sigma\Phi N_T$ (σ = reaction cross section, Φ = incoming flux density of projectiles, N_T= number of target atoms).
- If P is radioactive, its **decay rate** is given by: $-dN_P/dt = \lambda N_P$.
- Thus the **net production rate** is: $dN_P/dt = \sigma\Phi N_T - \lambda N_P$.
- Integration of the last equation gives: $N_P = (\sigma\Phi N_T / \lambda)\cdot (1-\exp(-\lambda t))$ for the number of atoms of nuclide P produced after irradiation time t.
- The corresponding activity of P is: $A = \lambda N_P = \sigma\Phi N_T\cdot (1-\exp(-\lambda t))$ **(1)**.
- The relation between N_T and the mass m of the element containing the target nuclide T is: $N_T= (N_{Av}/M)\, Hm$ **(2)** (N_{Av}=Avogadro's number, M=atomic mass of the target element, H=isotopic abundance of the nuclide T in the target element)
- Substitution of Eq.(2) in Eq.(1) gives: $A = \sigma\Phi H\, m\, (N_{Av}/M) \cdot (1-(½)^{t/t_{½}})$ ($t_{½}$=half life).

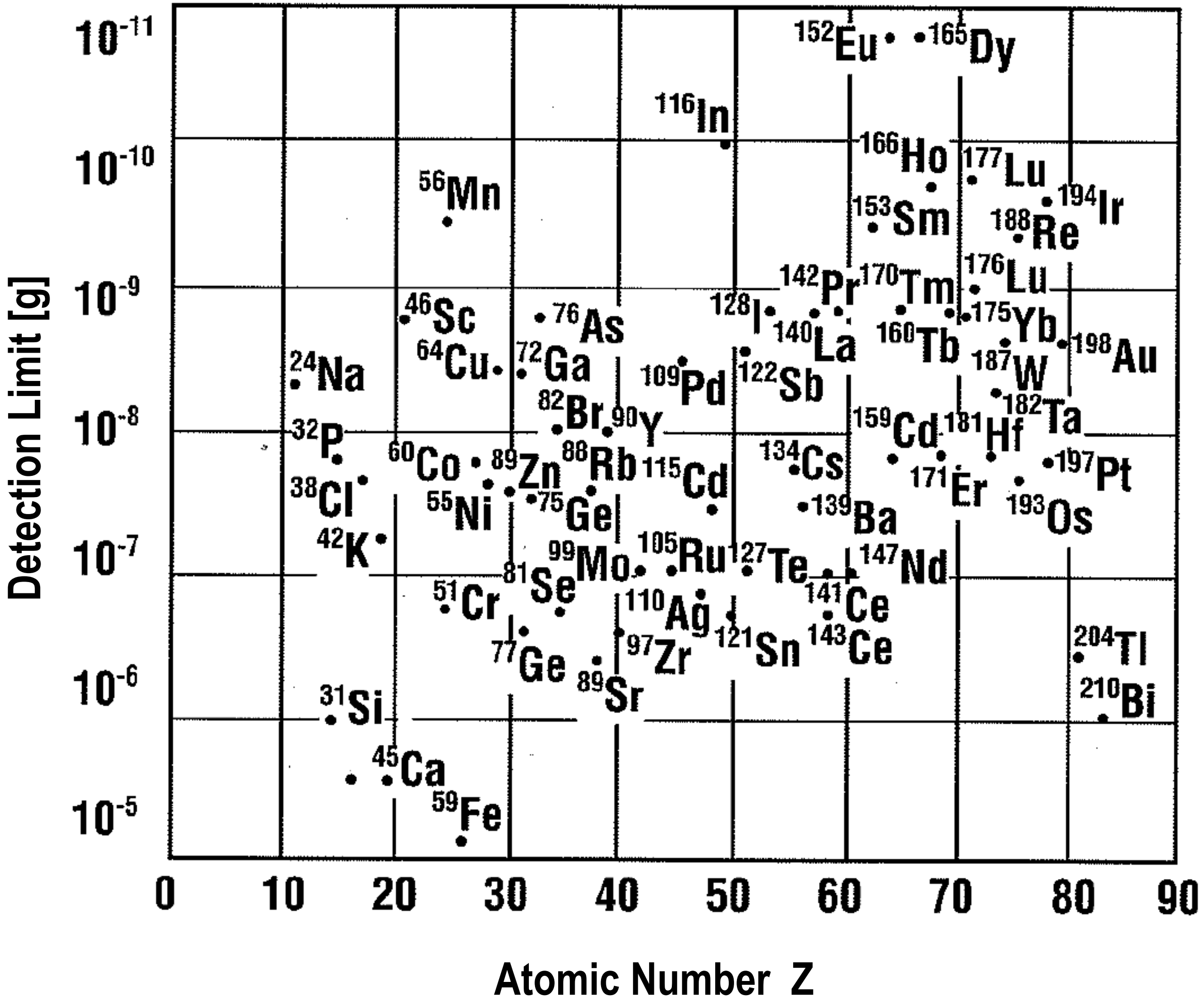
Activity as a Function of Irradiation Time



Basics: Principle of NAA

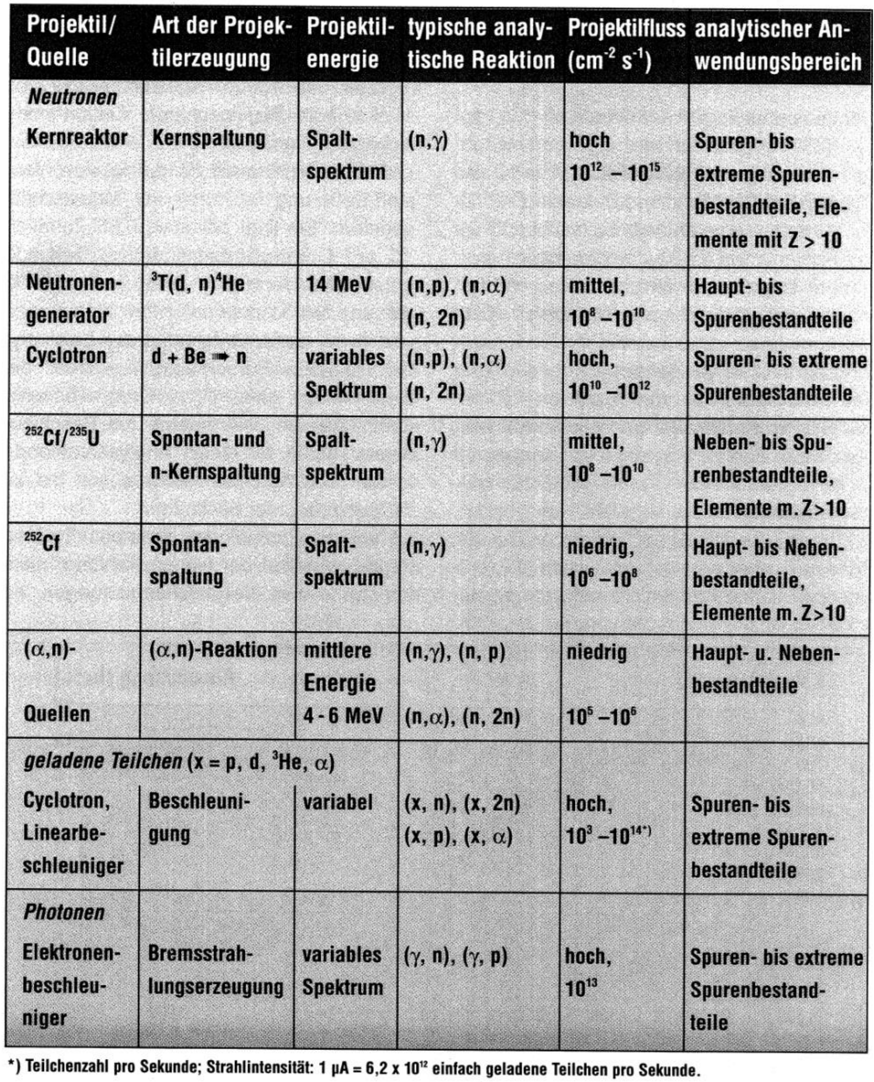
- NAA involves three steps:
  1. **Irradiation of the sample** at a known neutron flux in a research reactor, or with a neutron generator or portable neutron source. Mostly (n,γ) reactions will be induced and the produced nuclei P may be radioactive.
  2. Detection and **measurement of the level of radioactive isotopes** resulting from the neutron activation of the target material. To this end the energies of the emitted γ-rays have to measured **using a high-resolution γ-ray spectrometer** to distinguish the (often large number) of activated radionuclides.
  3. **Calculation of the concentration** of each activated component of the sample.
- The sensitivity of the analysis depends on the neutron absorption cross section of the isotopes of interest, the neutron flux density, and the effect of interference from other elements in the sample.

Detection limits by NAA



- For the diagram the following assumptions have been made:
  - Research reactor with a thermal neutron flux density of $\Phi=5\cdot10^{13}$n/cm^{2}/s.
  - Irradiation until saturation activity, but maximum one month.
  - 37Bq allow quantitative determination.

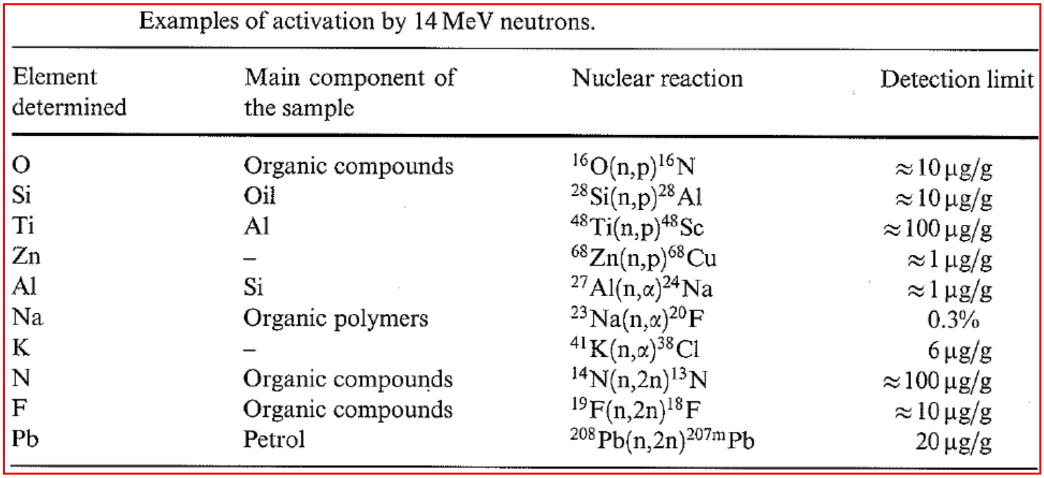
Overview: Activation Techniques and Sources



Projektil/ Quelle	Art der Projektilerzeugung	Projektilenergie	typische analytische Reaktion	Projektilfluss ($cm^{-2}\,s^{-1}$)	analytischer Anwendungsbereich
Neutronen					
Kernreaktor	**Kernspaltung**	**Spaltspektrum**	(n,γ)	**hoch** $10^{12}-10^{15}$	**Spuren- bis extreme Spurenbestandteile, Elemente mit Z > 10**
Neutronengenerator	$^{3}T(d,n)^{4}He$	**14 MeV**	(n,p), (n,α) $(n,2n)$	**mittel,** $10^{8}-10^{10}$	**Haupt- bis Spurenbestandteile**
Cyclotron	d + Be ➡ n	**variables Spektrum**	(n,p), (n,α) $(n,2n)$	**hoch,** $10^{10}-10^{12}$	**Spuren- bis extreme Spurenbestandteile**
$^{252}Cf/^{235}U$	**Spontan- und n-Kernspaltung**	**Spaltspektrum**	(n,γ)	**mittel,** $10^{8}-10^{10}$	**Neben- bis Spurenbestandteile, Elemente m. Z>10**
^{252}Cf	**Spontanspaltung**	**Spaltspektrum**	(n,γ)	**niedrig,** $10^{6}-10^{8}$	**Haupt- bis Nebenbestandteile, Elemente m. Z>10**
(α,n)-**Quellen**	(α,n)-**Reaktion**	**mittlere Energie 4 - 6 MeV**	(n,γ), (n,p) (n,α), $(n,2n)$	**niedrig** $10^{5}-10^{6}$	**Haupt- u. Nebenbestandteile**
geladene Teilchen **(x = p, d, ^{3}He, α)**					
Cyclotron, Linearbeschleuniger	**Beschleunigung**	**variabel**	(x,n), $(x,2n)$ (x,p), (x,α)	**hoch,** $10^{3}-10^{14\,*)}$	**Spuren- bis extreme Spurenbestandteile**
Photonen					
Elektronenbeschleuniger	**Bremsstrahlungserzeugung**	**variables Spektrum**	(γ,n), (γ,p)	**hoch,** 10^{13}	**Spuren- bis extreme Spurenbestandteile**

***) Teilchenzahl pro Sekunde; Strahlintensität: 1 μA = 6,2 x 10^{12} einfach geladene Teilchen pro Sekunde.**

- On the left: Overview of sources and techniques used in activation analysis.
- The high energy (14MeV) of the neutrons produced by $T(d,n)^{4}He$ reactions allows activation by (n,p), (n,α) or (n,2n)reactions. Examples are given below.

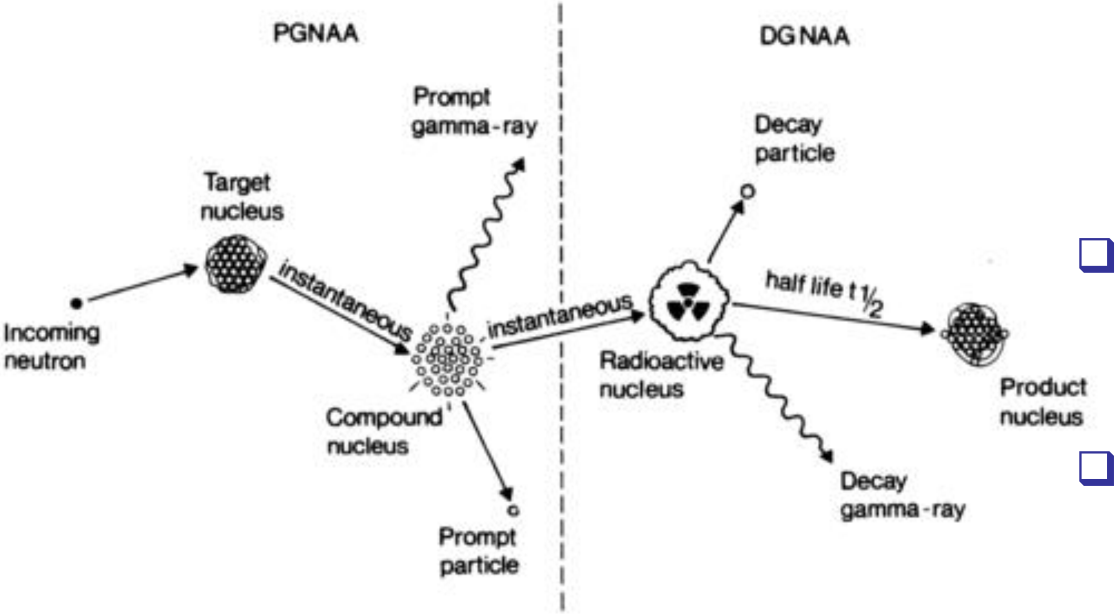


Examples of activation by 14 MeV neutrons.

Element determined	Main component of the sample	Nuclear reaction	Detection limit
O	Organic compounds	$^{16}O(n,p)^{16}N$	≈10 μg/g
Si	Oil	$^{28}Si(n,p)^{28}Al$	≈10 μg/g
Ti	Al	$^{48}Ti(n,p)^{48}Sc$	≈100 μg/g
Zn	–	$^{68}Zn(n,p)^{68}Cu$	≈1 μg/g
Al	Si	$^{27}Al(n,\alpha)^{24}Na$	≈1 μg/g
Na	Organic polymers	$^{23}Na(n,\alpha)^{20}F$	0.3%
K	–	$^{41}K(n,\alpha)^{38}Cl$	6 μg/g
N	Organic compounds	$^{14}N(n,2n)^{13}N$	≈100 μg/g
F	Organic compounds	$^{19}F(n,2n)^{18}F$	≈10 μg/g
Pb	Petrol	$^{208}Pb(n,2n)^{207m}Pb$	20 μg/g

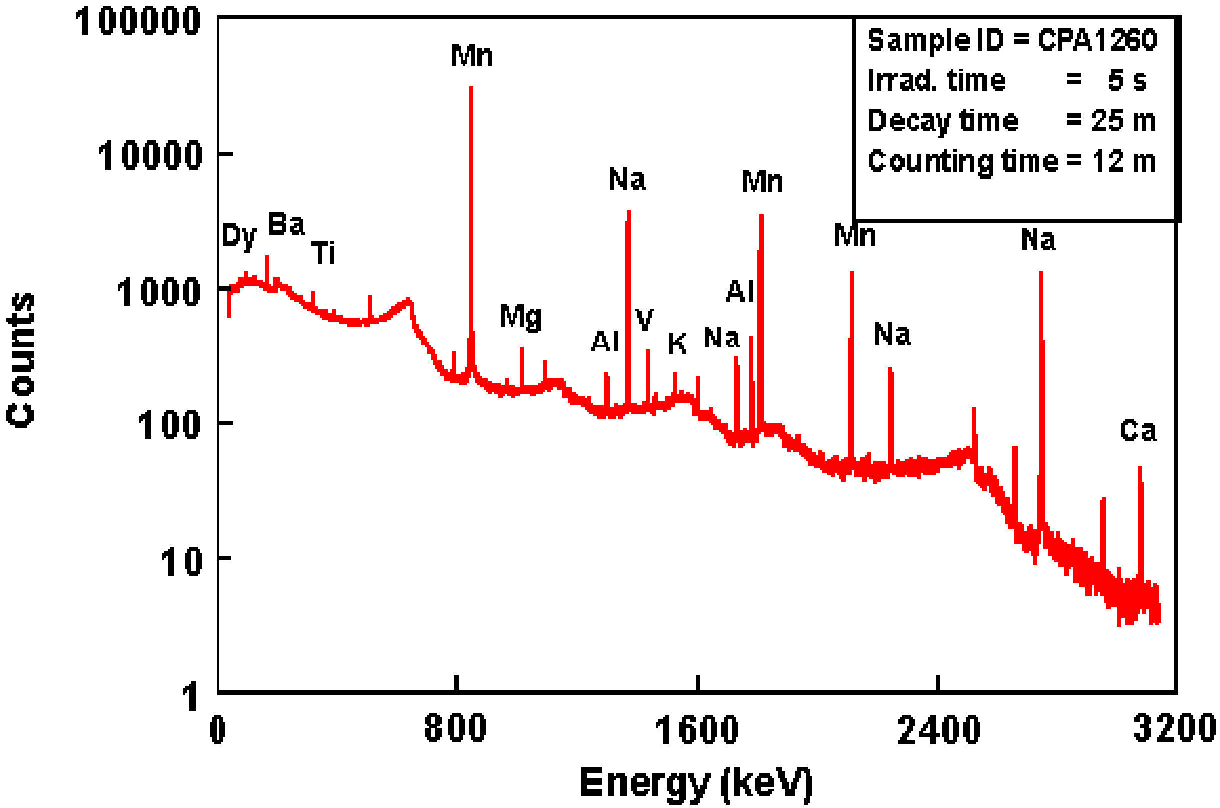
Variations of NAA According to Experimental Parameters

- ☐ The activation cross sections depend on the **kinetic energy of the neutrons E_N** which can be varied:
  - Standard NAA: $E_N < \sim 0.5\text{eV}$
  - Epithermal NAA (ENAA): $0.5\text{eV} < E_N < 0.1\text{MeV}$
  - Fast NAA (FNAA): $E_N > 0.1\text{MeV}$



- ☐ Depending whether the decay products (γ-rays or particles) are measured during irradiation (**prompt** γ) or at some time after irradiation (**delayed** γ) the terms **PGNAA** and **DGNAA** (or normal NAA) are used.
- ☐ PGNAA is generally applied when the half lives of the daughters are either too short or too long (especially stable isotopes!) for DGNAA. PGNAA is characterized by short irradiation and decay times.
- ☐ If NAA is conducted directly on irradiated samples in a more or less automated way, it is termed instrumental NAA (**INAA**).
- ☐ If the irradiated sample is subject to chemical separation to remove interfering species or to concentrate the radioisotope of interest, this is called Radiochemical NAA or (**RNAA**).

Detectors applied in NAA



- Detectors used in NAA mostly have to record and analyze γ-ray spectra. Thus scintillation and semiconductor detectors are mainly employed, often in combination with a multichannel analyzer operated by a computer and a program for peak search, energy calibration and radionuclide identification.
- The figure shows γ-ray spectra from a sample of neutron irradiated pottery obtained with a high purity Ge detector.
- In measurements the irradiation time, decay time, and counting time can be varied to optimize the signal to noise ratio.

The Main Fields of NAA-Applications

- Due to the high sensitivity, activation analysis is one of the most important methods for determination of micro-components, in particular trace elements, in materials of high purity, in water, in biological samples, and in minerals. It is mainly applied in/for:
  - Geo- and cosmo- chemistry (terrestrial and lunar samples, meteorites).
  - Art and archaeology (identification of the origin of the trace element pattern in very small samples).
  - Environmental samples (atmospheric aerosols, fly ash, water).
  - Biological samples (blood, organs, body fluid, hair, food).
- Examples of industrial applications are:
  - Coal and concrete processing companies use NAA to analyze the quality of the materials, PGNAA is routinely applied to monitoring the elemental composition of coal and other materials on conveyor belts.
  - Mining companies apply NAA to explore ores.

Two Selected Examples of NAA Applications:

- Napoleon Bonaparte died on May, 5th 1821. An Investigation of his hair 140 years later revealed that it contained 10.38 ppm arsenic in comparison to an arsenic level between 0.5 to 1.3 ppm in normal hair. The arsenic distribution over a hair length of 9 cm demonstrated that Napoleon had been administered several doses of arsenic within the four month before his death.

- In the area of Archeology the provenience of two huge statues of Pharaoh Amenophis III at the Nile river near Thebes could be identified. A comparison of the Eu, Fe, and Co content of the statue with those in the rocks of major Egyptian quarries showed that the monoliths (with a mass of 750t each) did not originate from Aswan, but came from the quarry Gebel Ahmar near Cairo, i.e., they were transported 650 km up-stream!

Example: NAA of Food Samples at State Lab. Basel-City: (1) Method

Characteristics of the activated nuclides

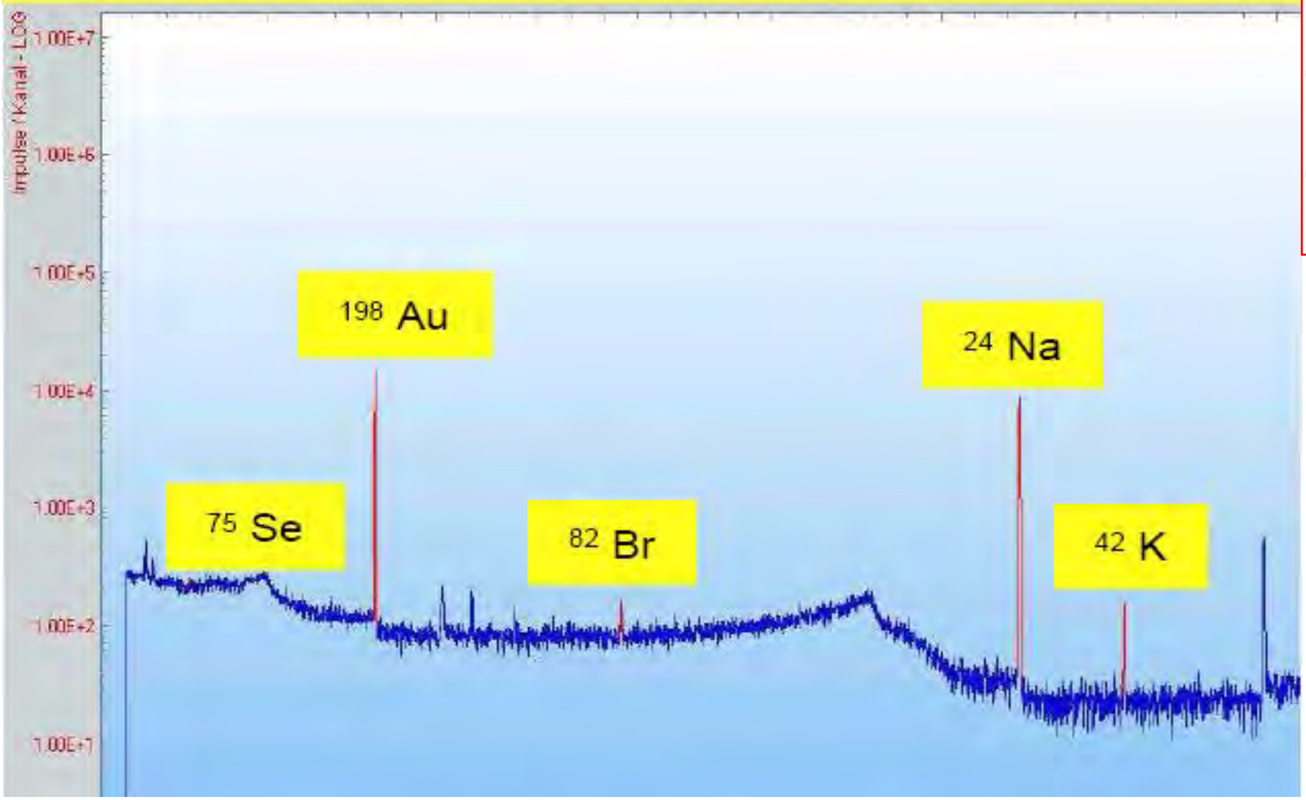
Element	activated nuclide	half-live	mean γ-Energy [keV]
Sodium	^{24}Na	14.96 h	1368.6
Potassium	^{42}K	12.36 h	1524.6
Manganese	^{56}Mn	2.58 h	846.8
Arsenic	^{76}As	26.32 h	559.1
Bromine	^{82}Br	35.28 h	776
Antimony	^{122}Sb	64.8 h	564.1
Gold	^{198}Au	64.56 h	411.8

Gold is used as an internal standard

- ☐ The use of methyl bromide (or bromomethane, CH_3Br) as a fumigant results in residues of bromine in food such as tea, vegetables and spices.
- ☐ At the State Laboratory Basel-City NAA was applied to determine the bromine content and major elements (such as sodium or potassium) of food.
- ☐ The sample preparation in vials comprised several steps including the activation for 30 minutes in a small reactor (type AGN-211-P, $\Phi=3.6\cdot10^{10}/\text{cm}^2/\text{s}$, P_{th}=2kW) at the Department of Physics in Basel.
- ☐ Finally a γ-spectrum was taken for 1000 seconds with a Ge-Detector.

Example: NAA of Food Samples at State Lab. Basel-City: (2) Results

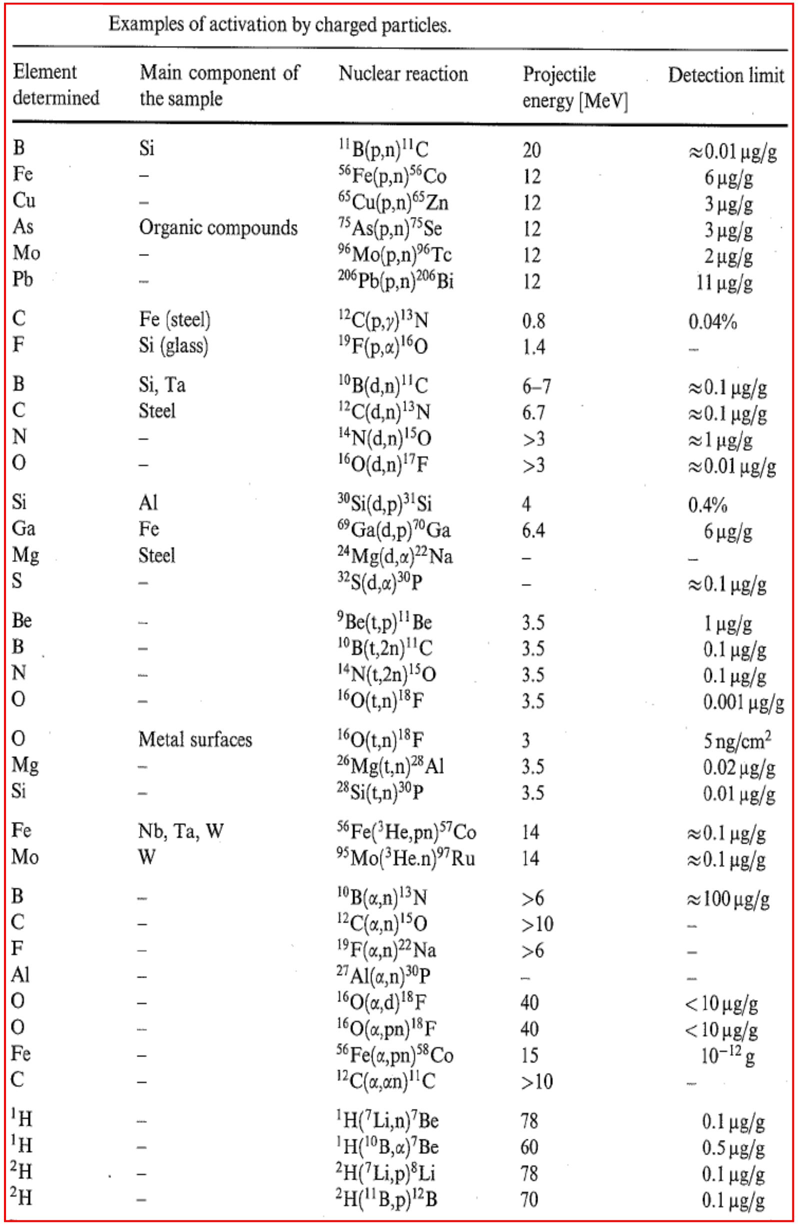
γ-Spectrum of an activated spice sample (curcuma with 5% sodium chloride) containing 100 mg/kg of bromine



food	tolerance value for bromide
Tea	50 mg/kg
Spice	100 mg/kg
Kakao beans	50 mg/kg
Coffee beans	50 mg/kg
Mushrooms	400 mg/kg
Cereals	50 mg/kg
Dried vegetables	100 mg/kg

- ☐ The analyzed spice sample contained 100mg/kg bromine and therefore certainly more methyl bromide than the allowed 100mg/kg !

Activation by Charged Particles

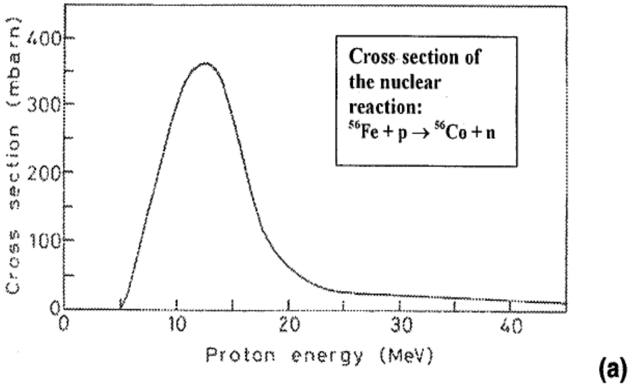


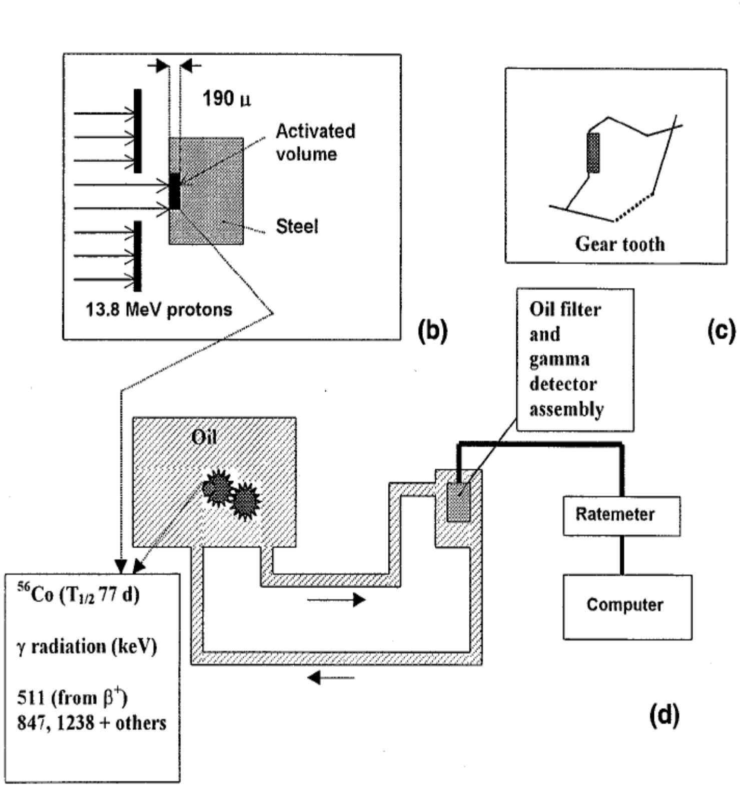
Examples of activation by charged particles.

Element determined	Main component of the sample	Nuclear reaction	Projectile energy [MeV]	Detection limit
B	Si	$^{11}B(p,n)^{11}C$	20	≈0.01 µg/g
Fe	–	$^{56}Fe(p,n)^{56}Co$	12	6 µg/g
Cu	–	$^{65}Cu(p,n)^{65}Zn$	12	3 µg/g
As	Organic compounds	$^{75}As(p,n)^{75}Se$	12	3 µg/g
Mo	–	$^{96}Mo(p,n)^{96}Tc$	12	2 µg/g
Pb	–	$^{206}Pb(p,n)^{206}Bi$	12	11 µg/g
C	Fe (steel)	$^{12}C(p,\gamma)^{13}N$	0.8	0.04%
F	Si (glass)	$^{19}F(p,\alpha)^{16}O$	1.4	–
B	Si, Ta	$^{10}B(d,n)^{11}C$	6–7	≈0.1 µg/g
C	Steel	$^{12}C(d,n)^{13}N$	6.7	≈0.1 µg/g
N	–	$^{14}N(d,n)^{15}O$	>3	≈1 µg/g
O	–	$^{16}O(d,n)^{17}F$	>3	≈0.01 µg/g
Si	Al	$^{30}Si(d,p)^{31}Si$	4	0.4%
Ga	Fe	$^{69}Ga(d,p)^{70}Ga$	6.4	6 µg/g
Mg	Steel	$^{24}Mg(d,\alpha)^{22}Na$	–	–
S	–	$^{32}S(d,\alpha)^{30}P$	–	≈0.1 µg/g
Be	–	$^{9}Be(t,p)^{11}Be$	3.5	1 µg/g
B	–	$^{10}B(t,2n)^{11}C$	3.5	0.1 µg/g
N	–	$^{14}N(t,2n)^{15}O$	3.5	0.1 µg/g
O	–	$^{16}O(t,n)^{18}F$	3.5	0.001 µg/g
O	Metal surfaces	$^{16}O(t,n)^{18}F$	3	5 ng/cm^2
Mg	–	$^{26}Mg(t,n)^{28}Al$	3.5	0.02 µg/g
Si	–	$^{28}Si(t,n)^{30}P$	3.5	0.01 µg/g
Fe	Nb, Ta, W	$^{56}Fe(^{3}He,pn)^{57}Co$	14	≈0.1 µg/g
Mo	W	$^{95}Mo(^{3}He.n)^{97}Ru$	14	≈0.1 µg/g
B	–	$^{10}B(\alpha,n)^{13}N$	>6	≈100 µg/g
C	–	$^{12}C(\alpha,n)^{15}O$	>10	–
F	–	$^{19}F(\alpha,n)^{22}Na$	>6	–
Al	–	$^{27}Al(\alpha,n)^{30}P$	–	–
O	–	$^{16}O(\alpha,d)^{18}F$	40	< 10 µg/g
O	–	$^{16}O(\alpha,pn)^{18}F$	40	< 10 µg/g
Fe	–	$^{56}Fe(\alpha,pn)^{58}Co$	15	10^{-12} g
C	–	$^{12}C(\alpha,\alpha n)^{11}C$	>10	–
^{1}H	–	$^{1}H(^{7}Li,n)^{7}Be$	78	0.1 µg/g
^{1}H	–	$^{1}H(^{10}B,\alpha)^{7}Be$	60	0.5 µg/g
^{2}H	–	$^{2}H(^{7}Li,p)^{8}Li$	78	0.1 µg/g
^{2}H	–	$^{2}H(^{11}B,p)^{12}B$	70	0.1 µg/g

- Charged particles must have enough energy to surmount the Coulomb barrier V_C between projectile and target: $V_C \sim Z_T Z_x e^2 / 4\pi\varepsilon_0 r$.
- In contrast to neutrons, the penetration depth of charged particles is relatively small. Thus only the surface layer of thicker samples is activated, which offers the possibility of surface analysis.
- E.g., ^{16}O can be determined by the reactions:
  - $^{16}O(p,\alpha)^{13}N$
  - $^{16}O(^{3}He,p)^{18}F$
  - $^{16}O(\alpha,d)^{18}F$
  - $^{16}O(t,n)^{18}F$
- The elements Be, B, C, F, which cannot be activated by thermal neutrons, can also be determined by charged particle activation.
- Also heavy ions like ^{7}Li, ^{10}B may be used for charged particle activation.

Example: Study of Wear Rate Using Thin Layer Activation

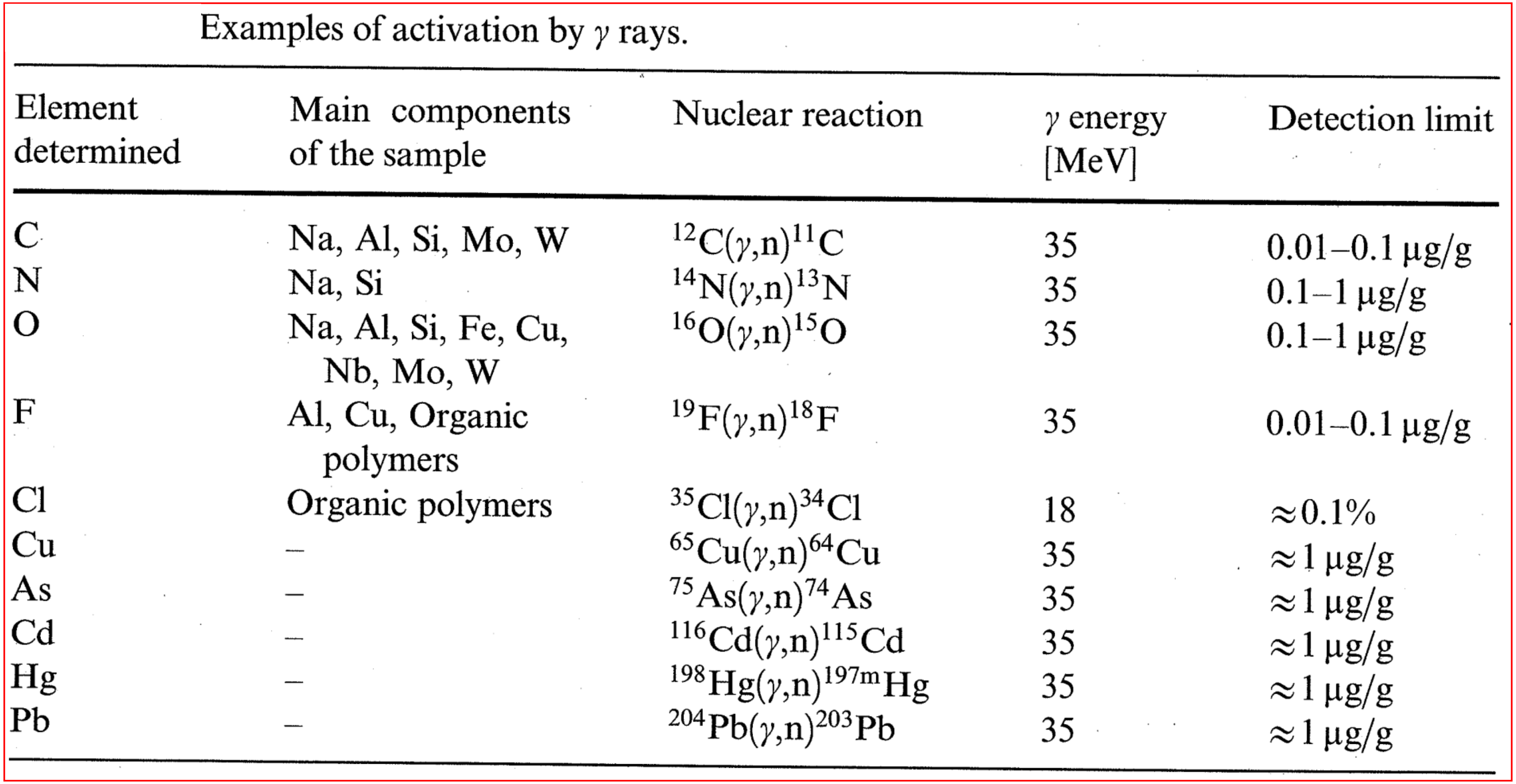




- Activation by protons can be used to study the wear rate of machine components made of iron. The analysis is based on the ^{56}Fe(p,n)^{56}Co reaction producing the radioisotope ^{56}Co with a half life of 77d and emitting γ-rays between 847 and 3253 keV.
- The principle is illustrated in the figure:
  - (a) Activation cross section as a function of the proton energy.
  - (b) Irradiation of a gear tooth, as shown in (c), with 13.8MeV protons.
  - (d) Measurement of the accumulation rate of wear debris on the filter. In another approach, a detector may be placed close to the component to monitor the material loss on the surface.
- As the monitoring does not interfere with the functioning of the machine, various parameters of the system may be investigated.

Activation by Photons

- Also photons can induce nuclear reactions, and photoexcitation (γ,γ’) may be applied to activation analysis.
- The **most important photo-induced reactions are (γ,n) and (γ,2n)** reactions, but also (γ,p) can be applied.



Examples of activation by γ rays.

Element determined	Main components of the sample	Nuclear reaction	γ energy [MeV]	Detection limit
C	Na, Al, Si, Mo, W	$^{12}C(\gamma,n)^{11}C$	35	0.01–0.1 μg/g
N	Na, Si	$^{14}N(\gamma,n)^{13}N$	35	0.1–1 μg/g
O	Na, Al, Si, Fe, Cu, Nb, Mo, W	$^{16}O(\gamma,n)^{15}O$	35	0.1–1 μg/g
F	Al, Cu, Organic polymers	$^{19}F(\gamma,n)^{18}F$	35	0.01–0.1 μg/g
Cl	Organic polymers	$^{35}Cl(\gamma,n)^{34}Cl$	18	≈0.1%
Cu	–	$^{65}Cu(\gamma,n)^{64}Cu$	35	≈1 μg/g
As	–	$^{75}As(\gamma,n)^{74}As$	35	≈1 μg/g
Cd	–	$^{116}Cd(\gamma,n)^{115}Cd$	35	≈1 μg/g
Hg	–	$^{198}Hg(\gamma,n)^{197m}Hg$	35	≈1 μg/g
Pb	–	$^{204}Pb(\gamma,n)^{203}Pb$	35	≈1 μg/g

Introduction to Nuclear Dating (ND)

- ☐ The laws of radioactive decay are the basis of chronology by nuclear methods.
- ☐ Rutherford was the first to stress the possibility of determining the age of uranium minerals from the amount of helium formed by radioactive decay.
- ☐ **ND is applied with great success in many fields of science**, mainly in:
  - Archaeology
  - Geology
  - Mineralogy
- ☐ Naturally occurring radionuclides (or environmental radionuclides) may be classified into two [three] subgroups according to their source:
  - **Cosmogenic radionuclides** are generated in the upper troposphere (0-10km) and lower stratosphere (10-30km) by the impact of cosmic radiation.
  - **Primordial isotopes** have been formed before the earth came into existence and have been decaying since then.
  - [**Fall-out products** resulting from past nuclear testing in the atmosphere.]

Basics: Nuclear Decay and Radioactive Equilibria (Supplement!)

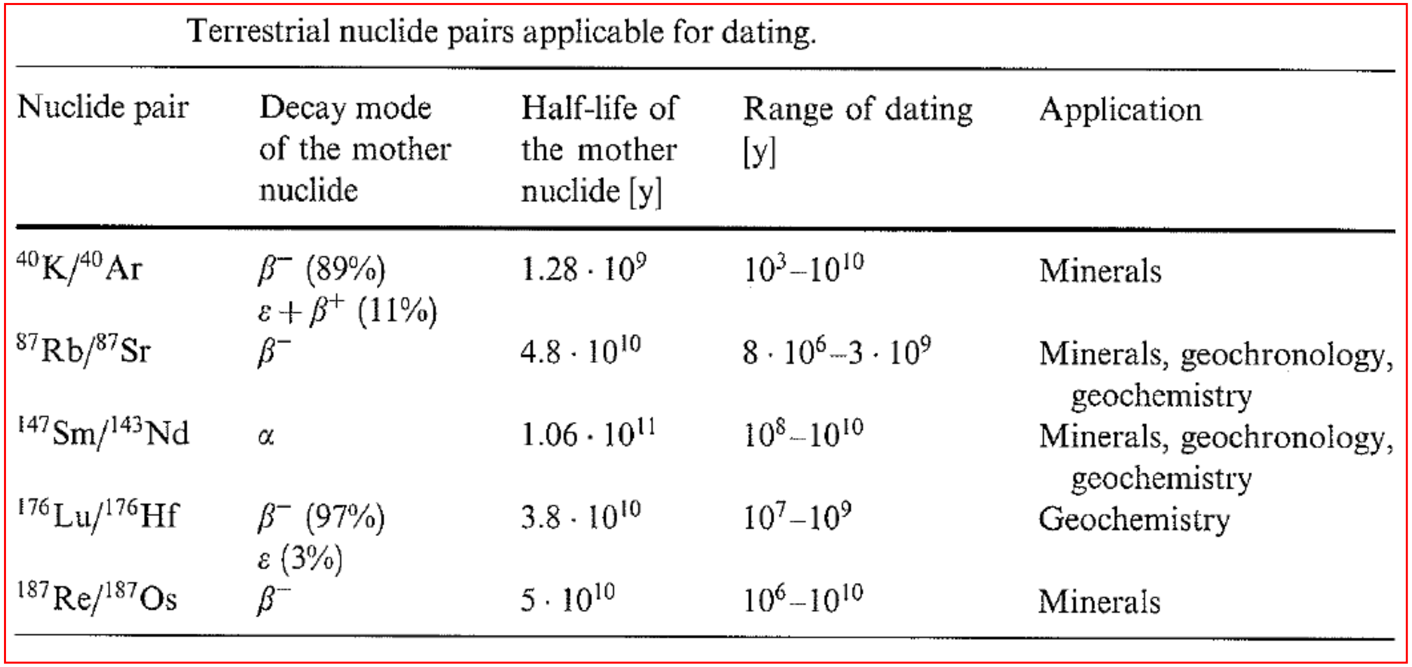
- ☐ From $dN/dt = -\lambda N$ we obtain by integration the decay law: **$N(t) = N^0 \cdot \exp(-\lambda t)$** with $\lambda = \ln 2/T_{1/2}$ and for the activity $A = -dN/dt = \lambda N^0 \cdot \exp(-\lambda t) = A^0 \cdot \exp(-\lambda t)$.
- ☐ In the simplest case, if one stable daughter atom (subscript 2) is formed per radioactive decay of the mother nuclide (subscript 1), the number of stable radiogenic atoms is: **$N_2 =$** $N_1^0 - N_1 = N_1^0 \cdot (1 - \exp(-\lambda t)) =$ **$N_1 \cdot (\exp(\lambda t) - 1)$**. Thus, for dating N_2 and N_1 must be determined.
- ☐ If several (n) stable atoms are produced per radioactive decay of the mother nuclide (i.e. in a decay series), as in the case of ^4He (α) formed by decay of ^{238}U, ^{232}Th, ^{235}U, the number of stable radiogenic atoms is: **$N_2(\alpha) =$** $n(N_1^0 - N_1) = nN_1^0 \cdot (1 - \exp(-\lambda t)) =$ **$nN_1 \cdot (\exp(\lambda t) - 1)$**.
- ☐ In general, at time t=0 stable nuclides of the daughter may already be present, and the total number of atoms of type 2 will be given by: **$N_2 = N_2^0 + N_1 \cdot (\exp(\lambda t) - 1)$ (3)**. Then, for dating, the three unknowns N_2, N_1, N_2^0 must be determined.
- ☐ In a radioactive decay chain $N_1 \rightarrow N_2 \rightarrow N_3 \rightarrow \ldots$ after about 10 half-lives of the longest lived daughter nuclide **radioactive equilibrium** (secular equilibrium) is established and the following equations hold: **$\lambda_1 N_1 = \lambda_2 N_2 = \lambda_3 N_3 = \ldots = \text{const.}$** (or $A_1 = A_2 = \ldots = \text{const.}$).

Nuclear Dating (ND): Overview

- ☐ In principle all naturally occurring isotopes can be used for dating. The time scale of applicability depends on the half-life. Most accurate results are obtained if the unknown age and the half-life $T_{½}$ of the radionuclide are of the same order. In general: $0.1 \cdot T_{½} < \text{age} < 10 \cdot T_{½}$.
- ☐ The following **methods of nuclear dating** can be distinguished:
  - Measurement of cosmogenic radionuclides.
  - Measurement of terrestrial mother/daughter nuclide pairs.
  - Measurement of members of the natural decay series.
  - Measurement of isotope ratios of stable radiogenic isotopes.
  - Measurement of radioactive disequilibria.
  - Measurement of fission tracks.
- ☐ For all methods it is important whether the systems are closed or open.
- ☐ The main problems with application of cosmogenic radionuclides are:
  - The knowledge of the production rate during the time span of interest.
  - The possibility of interferences (e.g. by nuclear explosions).

Terrestrial Mother/Daughter Nuclide Pairs (1)

- ❑ Terrestrial mother/daughter nuclide pairs suitable for dating are listed in the table.
- ❑ In principle, the three unknowns N_2, N_1, N_2^0 in the equation **$N_2 = N_2^0 + N_1 \cdot (\exp(\lambda t) - 1)$** must be determined, however in special cases N_2^0 may be neglected (or the calculated age may be considered an upper limit).
- ❑ In practice, two approaches for the determination of N_2 and N_1 are used:
  - **independent determination**, which can be achieved by various analytical methods (e.g., isotopic dilution),
  - or **simultaneous determination** of N_2 and N_1 **by mass spectrometry** (**MS**).



Terrestrial nuclide pairs applicable for dating.

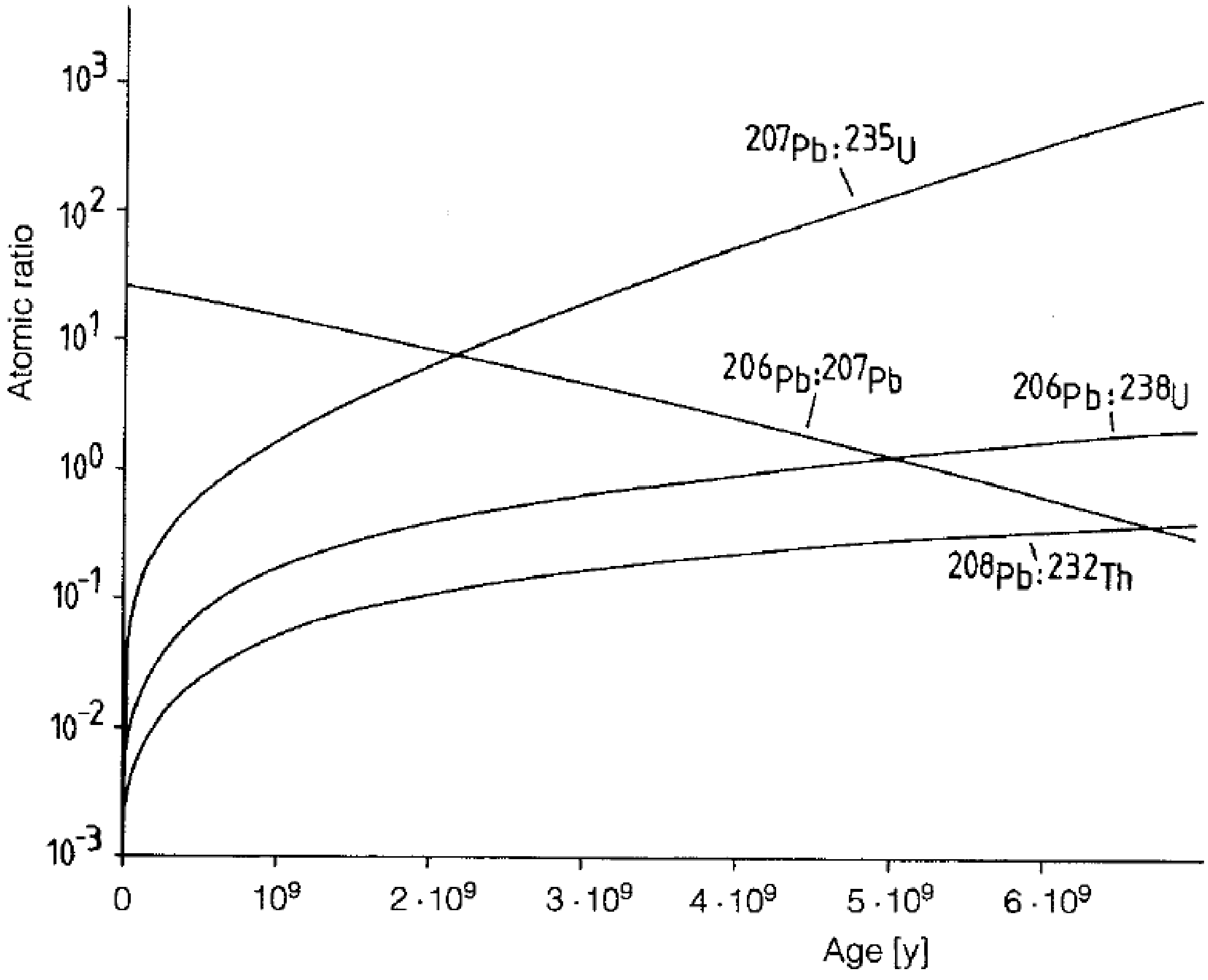
Nuclide pair	Decay mode of the mother nuclide	Half-life of the mother nuclide [y]	Range of dating [y]	Application
$^{40}K/^{40}Ar$	β^- (89%) $\varepsilon + \beta^+$ (11%)	$1.28 \cdot 10^9$	10^3–10^{10}	Minerals
$^{87}Rb/^{87}Sr$	β^-	$4.8 \cdot 10^{10}$	$8 \cdot 10^6$–$3 \cdot 10^9$	Minerals, geochronology, geochemistry
$^{147}Sm/^{143}Nd$	α	$1.06 \cdot 10^{11}$	10^8–10^{10}	Minerals, geochronology, geochemistry
$^{176}Lu/^{176}Hf$	β^- (97%) ε (3%)	$3.8 \cdot 10^{10}$	10^7–10^9	Geochemistry
$^{187}Re/^{187}Os$	β^-	$5 \cdot 10^{10}$	10^6–10^{10}	Minerals

- ❑ The age of potassium containing minerals can be extracted by evaluation of the nuclide pair $^{40}K/^{40}Ar$. Here N_2 and N_1 are determined separately:
  - Concentration of ^{40}K is obtained by an analytical method.
  - For ^{40}Ar the isotope dilution method is applied.

Terrestrial Mother/Daughter Nuclide Pairs (2): Simultaneous Determination

- Simultaneous determination of N_2 and N_1 is conveniently performed by use of a stable non-radiogenic nuclide as reference nuclide (r) and measurement of the ratios N_2/N_r and N_1/N_r . Dividing Eq. (3) by N_r we obtain:
  - $N_2/N_r = N_2^0/N_r + N_1/N_r \cdot (\exp(\lambda t) - 1)$ (4)
- For samples of the same age (or constant value of t) Eq. (4) can be applied iteratively (a piece of rock often contains different minerals with various N_2/N_1 ratios), and a plot of N_2/N_r versus N_1/N_r gives a straight line with slope $(\exp(\lambda t)-1)$ intersecting the ordinate at N_2^0/N_r . Such a plot is called isochrone. Thus all three unknowns can be determined.
- Finally, according to Eq. (4) the age of the sample is given by:
  - $t = (T_{1/2} / \ln 2) \ln [1 + (N_2/N_r - N_2^0/N_r) / (N_1/N_r)]$
- Simultaneous determination of mother and daughter nuclide by MS is applied in the $^{87}Rb/^{87}Sr$ method, and stable ^{86}Sr serves as a reference nuclide. This method is considered nowadays the most reliable technique for dating rock.
- For dating of very old minerals the $^{147}Sm/^{143}Nd$ method is used. Mother and daughter nuclides are also determined simultaneously by MS, and ^{144}Nd serves as a reference.

Natural Decay Series (1)



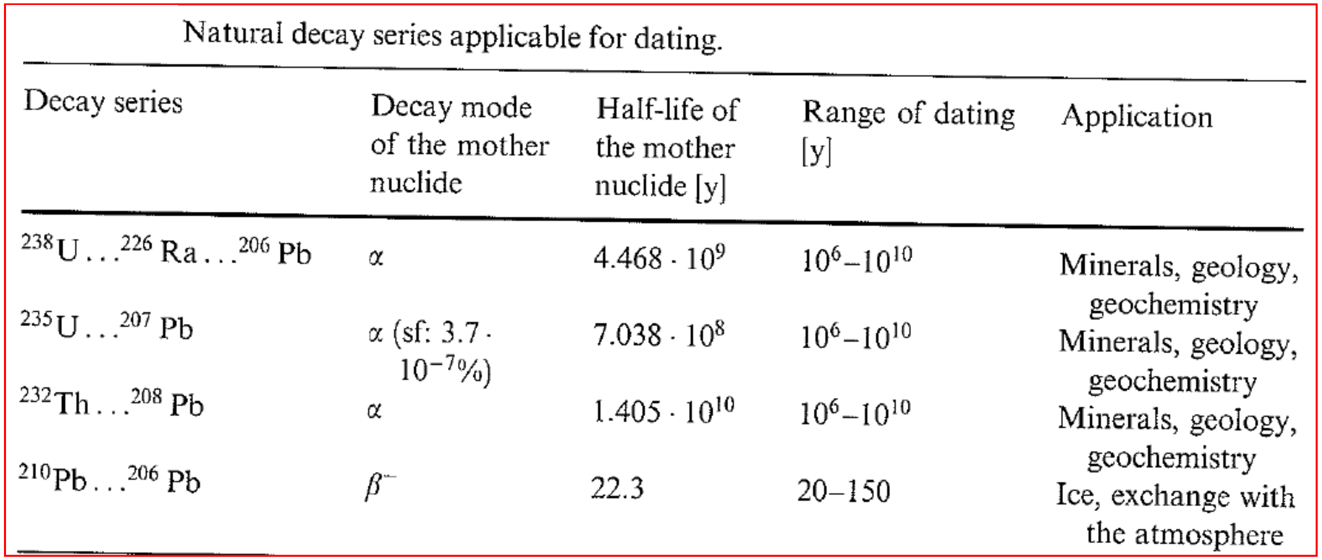
Radiogenic Pb isotopes: atomic ratios as a function of age.

- ☐ Also the isotopes of the three natural decay series can be applied for nuclear dating.
- ☐ The atomic ratios $^{206}Pb:^{238}U$, $^{207}Pb:^{235}U$ and $^{208}Pb:^{232}Th$ due to radioactive decay of the mother nucleus are plotted as a function of age, **provided that no losses have occurred**.
- ☐ The attainment of radioactive equilibria in the 3 decay chains depends on the longest-lived daughter nuclides in the series. These are:
  - ^{234}U, $T_{½} = 2.455 \cdot 10^5 a$
  - ^{231}Pa, $T_{½} = 3.276 \cdot 10^4 a$
  - ^{228}Ra, $T_{½} = 5.75 a$
- ☐ After about 10 half-lives of these, equilibrium is established.
- ☐ ^{204}Pb is not radiogenic and thus can be used as a reference nuclide.

Natural Decay Series (2)

❑ Three kinds of systems can be distinguished:

- **Open systems**: these lose parts of the members of the decay chains or the radiogenic Pb by diffusion or recrystallization processes. Dating of those systems encounters severe difficulties, and special correction methods must be used.
- **Closed systems**: or systems for which loss of members in decay chain can be neglected. Eq.(4) gives:
  - $({}^{206}Pb/{}^{204}Pb) = ({}^{206}Pb/{}^{204}Pb)_0 + ({}^{238}U/{}^{204}Pb)(\exp((\lambda(238)t) - 1)$
  - $({}^{207}Pb/{}^{204}Pb) = ({}^{207}Pb/{}^{204}Pb)_0 + ({}^{235}U/{}^{204}Pb)(\exp((\lambda(235)t) - 1)$ **(5)**
  - $({}^{208}Pb/{}^{204}Pb) = ({}^{208}Pb/{}^{204}Pb)_0 + ({}^{232}Th/{}^{204}Pb)(\exp((\lambda(232)t) - 1)$
- Systems for which loss of members in decay chain can be neglected, but which suffered from loss of the mother (e.g., uranium can be lost due to oxidation to UO_2^{2+} and dissolution). Here the Pb/Pb method can be applied (discussed later).



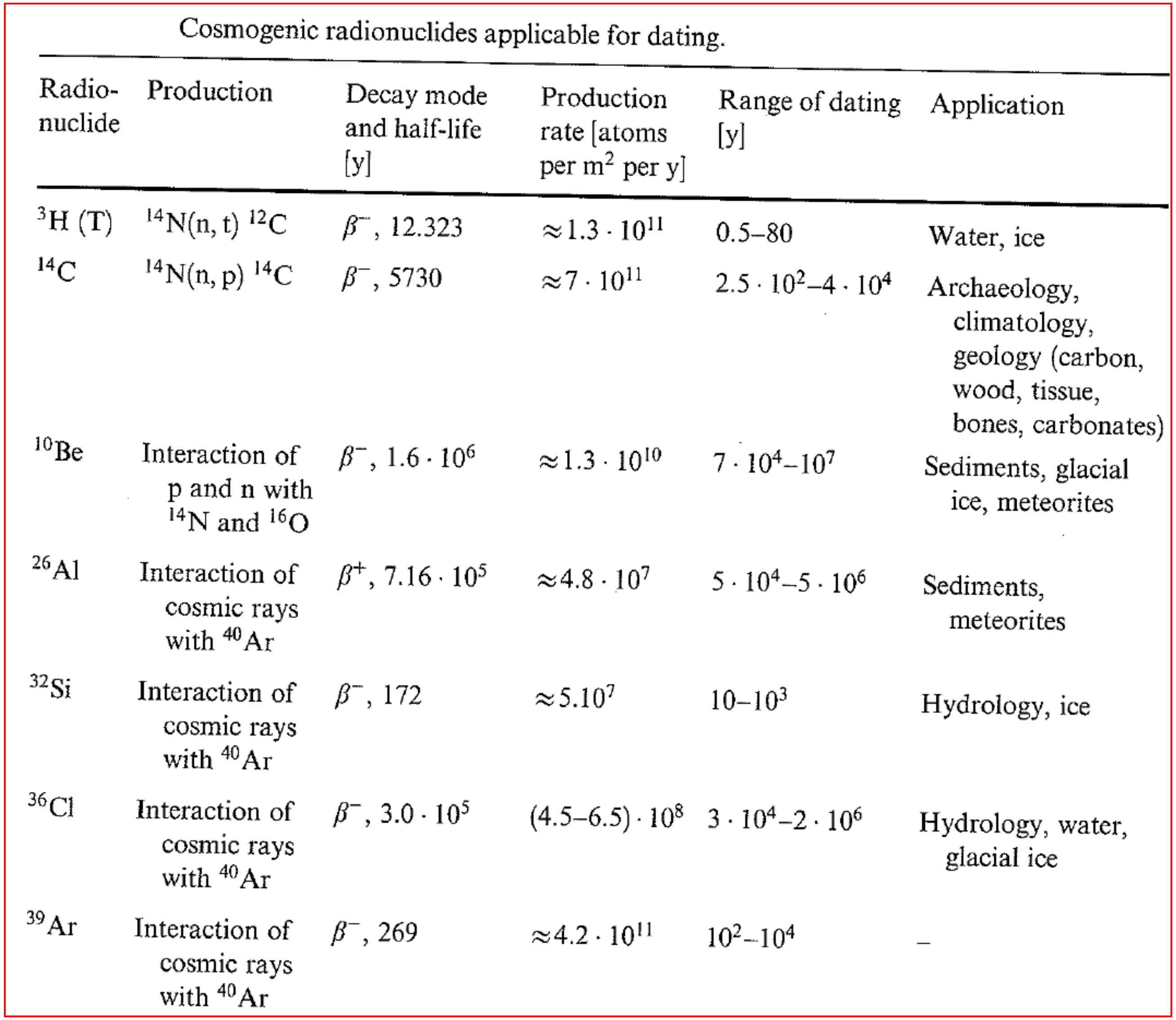
Natural decay series applicable for dating.

Decay series	Decay mode of the mother nuclide	Half-life of the mother nuclide [y]	Range of dating [y]	Application
${}^{238}U \ldots {}^{226}Ra \ldots {}^{206}Pb$	α	$4.468 \cdot 10^9$	10^6–10^{10}	Minerals, geology, geochemistry
${}^{235}U \ldots {}^{207}Pb$	α (sf: $3.7 \cdot 10^{-7}$%)	$7.038 \cdot 10^8$	10^6–10^{10}	Minerals, geology, geochemistry
${}^{232}Th \ldots {}^{208}Pb$	α	$1.405 \cdot 10^{10}$	10^6–10^{10}	Minerals, geology, geochemistry
${}^{210}Pb \ldots {}^{206}Pb$	β^-	22.3	20–150	Ice, exchange with the atmosphere

❑ In early stages of dating measurements of ${}^4He$ formed by α-decay in the natural decay series has been applied.

❑ The applications of the natural decay series for dating are summarized in the table.

Cosmogenic Radionuclides: Overview



Cosmogenic radionuclides applicable for dating.

Radio-nuclide	Production	Decay mode and half-life [y]	Production rate [atoms per m^2 per y]	Range of dating [y]	Application
^{3}H (T)	$^{14}N(n, t)\ ^{12}C$	β^-, 12.323	$\approx 1.3 \cdot 10^{11}$	0.5–80	Water, ice
^{14}C	$^{14}N(n, p)\ ^{14}C$	β^-, 5730	$\approx 7 \cdot 10^{11}$	$2.5 \cdot 10^2 – 4 \cdot 10^4$	Archaeology, climatology, geology (carbon, wood, tissue, bones, carbonates)
^{10}Be	Interaction of p and n with ^{14}N and ^{16}O	β^-, $1.6 \cdot 10^6$	$\approx 1.3 \cdot 10^{10}$	$7 \cdot 10^4 – 10^7$	Sediments, glacial ice, meteorites
^{26}Al	Interaction of cosmic rays with ^{40}Ar	β^+, $7.16 \cdot 10^5$	$\approx 4.8 \cdot 10^7$	$5 \cdot 10^4 – 5 \cdot 10^6$	Sediments, meteorites
^{32}Si	Interaction of cosmic rays with ^{40}Ar	β^-, 172	$\approx 5.10^7$	$10 – 10^3$	Hydrology, ice
^{36}Cl	Interaction of cosmic rays with ^{40}Ar	β^-, $3.0 \cdot 10^5$	$(4.5–6.5) \cdot 10^8$	$3 \cdot 10^4 – 2 \cdot 10^6$	Hydrology, water, glacial ice
^{39}Ar	Interaction of cosmic rays with ^{40}Ar	β^-, 269	$\approx 4.2 \cdot 10^{11}$	$10^2 – 10^4$	–

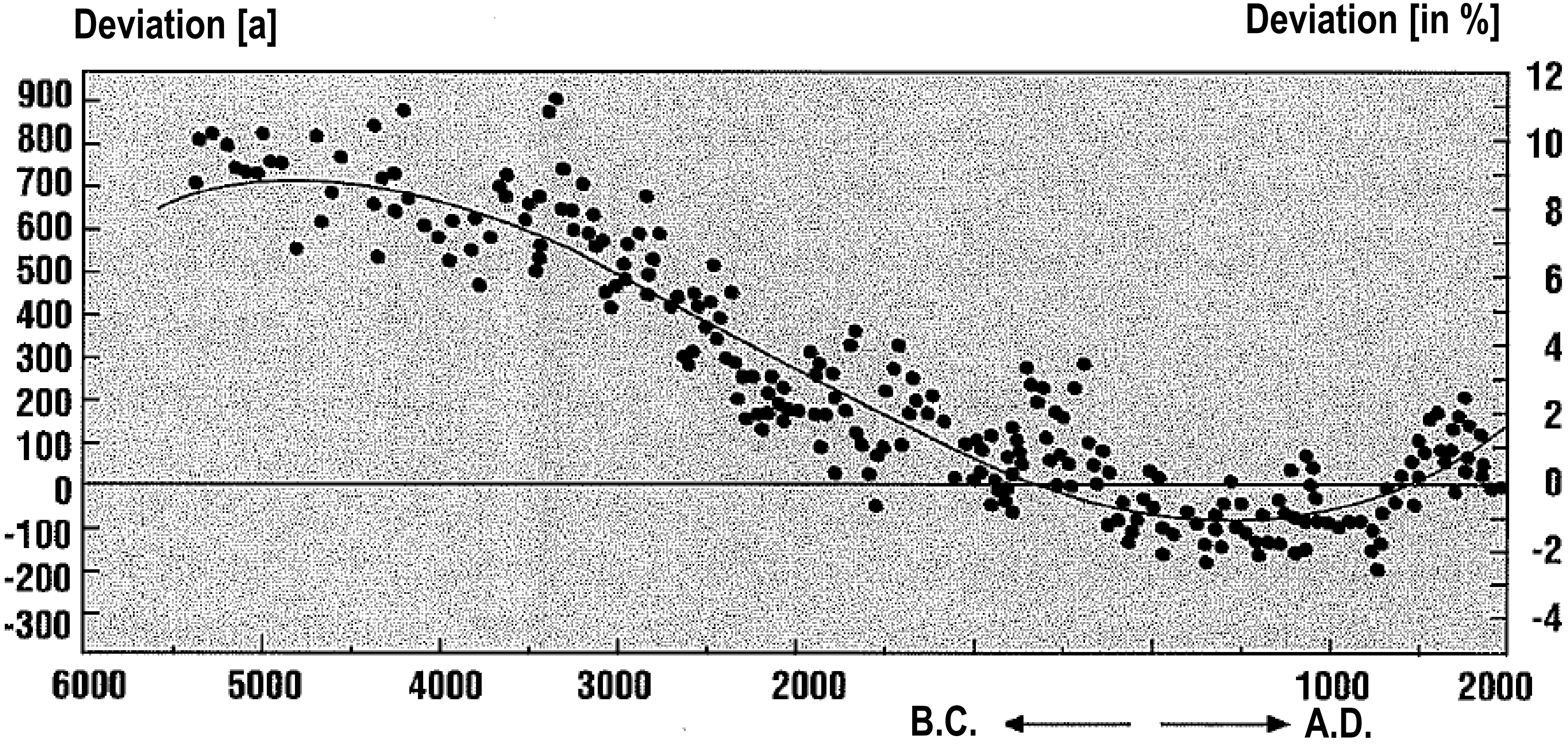
- All cosmogenic radio-nuclides applicable for dating are listed in the table. Their production rate is constant, if the intensity of cosmic rays is constant.
- The cosmogenic radio-nuclides take part in the various natural cycles on the surface of the earth, like the water cycle and the CO_2 cycle, and they are incorporated in various organic and inorganic products of these cycles, such as plants, sediments and glacial ice. If no exchange takes place, the activity of the radionuclides is a measure of their age.

Radiocarbon Dating (1): Basics

- ☐ Carbon has two stable isotopes ^{12}C (98.9%) and ^{13}C (1.1%). Furthermore there are tiny amounts of the radionuclide ^{14}C (β-emitter, $T_{½}$ = 5730a), which is produced by cosmic radiation neutrons hitting ^{14}N nuclei in the earth's atmosphere: $^{14}N(n,p)^{14}C$.
- ☐ (Today) the production rate of ^{14}C is 2.2 atoms per cm^2 earth surface and second. The ^{14}C atoms chemically react with the oxygen in the air to form CO_2.
- ☐ Plants take up atmospheric carbon dioxide by photosynthesis, and are eaten by animals and humans, so every living thing is constantly exchanging ^{14}C with its environment as long as it lives. Once it dies this exchange stops, and the concentration of ^{14}C gradually decreases due to $^{14}C(\beta^-)^{14}N$.
- ☐ Thus the age of organic samples can be determined by "**Radiocarbon Dating**".
- ☐ The upper limit for the age of carbonaceous materials determined with the radiocarbon method is about 60,000 years.

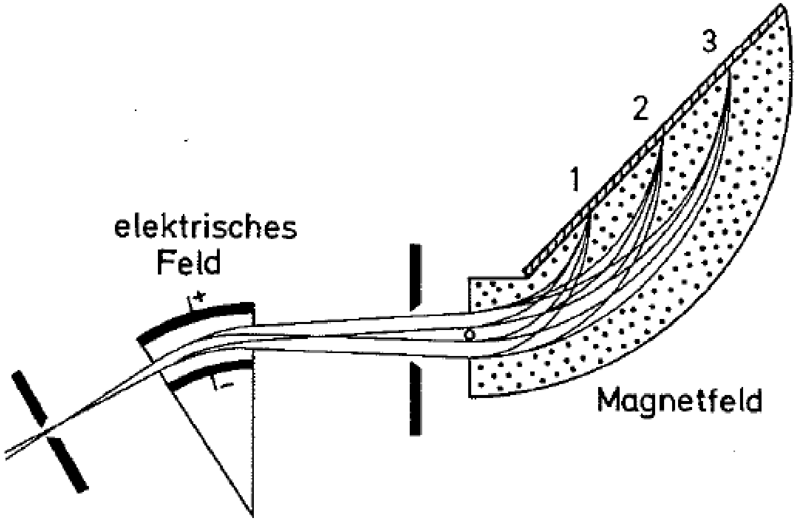
Radiocarbon Dating (2): Calibration Methods

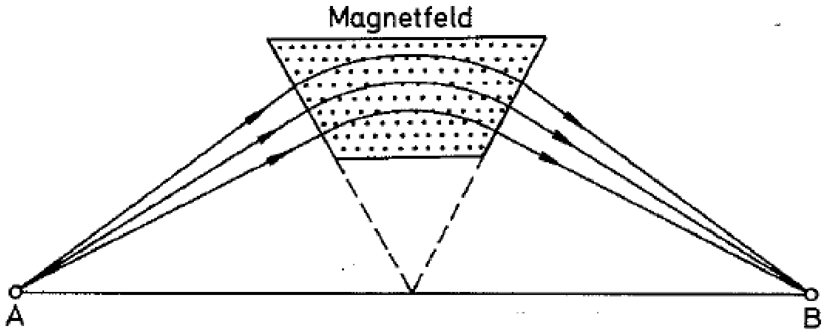
- The level of atmospheric ^{14}C has not been strictly constant over the last 60,000 years. Variations occurred due to: (1) Changes in the intensity of the cosmic radiation, (2) Human activities, especially massive burning of fossil fuels, and atomic bomb tests in the atmosphere between 1950-1960.
- Thus calibration is needed, which can be done by independent dating via, e.g., tree growth rings, ice cores, deep ocean sediment cores. Thus “radiocarbon years” can be correctly translated to calendar years, figure shows difference between the two.



Radiocarbon Dating (3): Measurement and AMS

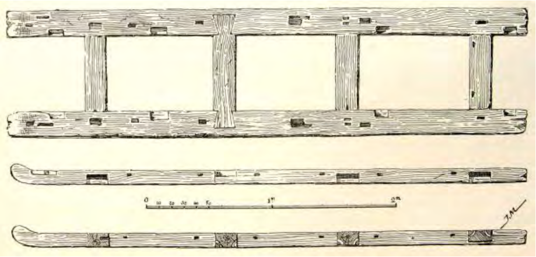
- ^{14}C concentrations have traditionally been measured with proportional counters and liquid scintillation detectors. With this equipment ages up to about 10,000 year could be determined.
- Sensitivity has been greatly increased by the use of **accelerator-based mass spectrometers (AMS)**. With this method all the ^{14}C atoms can be counted directly, contrary to the traditional methods, which only detect the decaying ^{14}C atoms.
- The principle of a mass spectrometer to measure the e/m-ratio (charge divided by mass) of radionuclides is illustrated in the figure: After the radionuclide has been ionized and accelerated in an electric field (accelerator part), it is directed through a capacitor (another electric field perpendicular to the direction of flight), which is the so called **energy-filter**, and finally runs through a magnetic field, which is a **momentum-filter**. The combination of the two filters allows the separation of radionuclides with different e/m-ratios, which are finally registered by detectors at different locations 1,2,3,…Also shown is a focusing magnet. Via AMS isotope ratios down to the order of about 10^{-15} can be measured, corresponding to ages ~ 60,000 years.

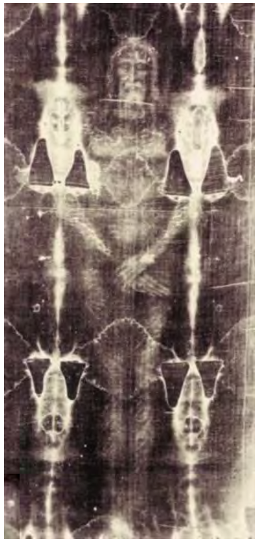




Radiocarbon Dating (4): Examples

- ☐ The plank pieces of the funeral ship of the Egypt King Sesostris III were determined to be 3800 years old.
- ☐ To the old Peruvian hempen rope an age of 3600 years could be assigned.
- ☐ The Qumram scrolls were determined to be 1900 years old.
- ☐ The “Shroud of Turin” could be dated to the middle ages (between 1260 and 1390 AD).



Other Cosmogenic Radionuclides

- ☐ **Tritium** atoms formed in the stratosphere are transformed into HTO and enter the water cycle. Thus samples of groundwater, polar ice and old wine can in principle be dated with tritium. Problems arise from the tritium carried into the atmosphere by thermonuclear explosions around the year 1960.
- ☐ **^{10}Be** can be found in concentrations of (3-7)· 10^4 atoms per gram of antarctic ice.
- ☐ **^{26}Al** is mainly used to date meteorites and samples from the surface of the moon.
- ☐ **^{32}Si** is applicable for dating of groundwater, ocean water, glacier ice, polar ice and sediments. Its half-life of 172 years offers some advantages over other radionuclides with respect to dating of ages up to about 1000 years.
- ☐ As **^{36}Cl** stays predominantly in the aqueous phase, it is mainly applied for hydrological studies, e.g. on the time of transport of water within deep layers, the rate of erosion processes, and the age of deep groundwater.

Ratios of Stable Isotopes / Radioactive Disequilibria / Fission Tracks

- A measurement of the **ratios of stable Pb isotopes** alone (**Pb/Pb method**) offers the possibility of dating without knowledge of the concentration of the mother nuclides U and Th. To this end the Eqs. (5) (on slide 24) must be combined with the knowledge of the ^{235}U:^{238}U ratio as a function of time and the fact that the Th:U ratio is practically constant for minerals of the same genesis.
- **Radioactive disequilibria**: by measuring the decay of the separated daughter nuclide or the growth of the daughter nuclide in the phase containing the mother nuclide, the time can be determined at which the separation took place. This provides information about separation processes in minerals and ores and about formation of sediments in oceans or lakes.
- **Fission tracks** are observed in solids due to spontaneous or neutron-induced fission of heavy nuclei. The primary tracks can be made visible under an optical microscope by treatment with chemicals, by which track diameters of the order of 0.1 to 0.5 μm are obtained. The method is the same as that used with track detectors. The length of the fission tracks depends on the nature of the minerals and varies between 10 and 20 μm. With respect to dating, the only important source of fission tracks is spontaneous fission of ^{238}U. Examples: High fission track densities were found in the vicinity of nuclear explosions and at the natural reactors at Oklo.

Summary

- **Neutron Activation Analysis is a widely applied method to determine the concentration of elements in a vast amount of materials.** Its advantages are:
  - It does not destroy the sample (**non-destructive analysis**) and hence:
    - can be used to analyze works of art or historical artifacts
    - is not subject to sample preparation or after-treatment (which both may introduce unwanted impurities)
  - It has a very **high sensitivity**, and thus gives **very accurate results**.
  - A large number of trace elements (up to about 70) can be determined simultaneously.
  - It is generally recognized as the **"referee method"** of choice when new procedures are being developed or other methods yield results that do not agree (**blank-free technique**).
- **Nuclear Dating is applied with great success in many fields of science**, mainly in:
  - Archaeology
  - Geology
  - Mineralogy
- In principle all naturally occurring isotopes (cosmogenic and primordial radionuclides) can be used for dating. However **radiocarbon dating** (**^{14}C-method**) plays the most important role, because it can be applied to date organic samples.
- Sensitivity has been greatly increased by the use of **AMS**.

Literature / WWW-references

- ☐ G.C. Lowenthal, P.L. Airey, *"Practical Applications of Radioactivity and Nuclear Reactions"*, Cambridge University Press (2001) **Chapter 7 and 9**
- ☐ K.H. Lieser, *"Nuclear and Radiochemistry"*, WILEY-VCH (2nd edition, 2001)
- ☐ Home page of the PSI Activation Service: http://neutra.web.psi.ch/irradiation.htm
- ☐ ANS Public Information web site: http://www.aboutnuclear.org