

The real alchemy or Chemical analysis with neutrons

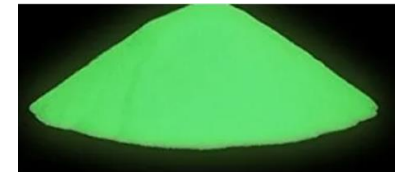
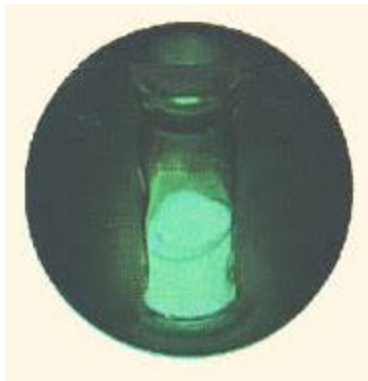
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Garching, Germany

MLZ is a cooperation between:

- Were trying to make gold
- In general to transform chemical elements
- On the way they invented many techniques and equipment of the future chemistry
- Sometimes produced other valuable substances like medicine, china (porcelain), ...
- Transmutation needs transformation of nucleus



Artistic approach to the Curies and radium



1898 Christmas

- Marie and Pierre Curie



Radioactivity



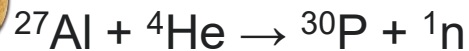
New elements: Ra, Po

1934

- Irène and Frédéric Joliot-Curie



Artificial radioactivity



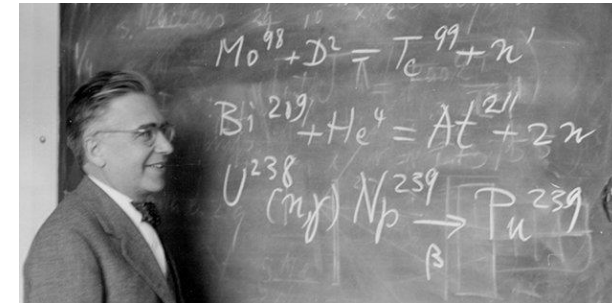
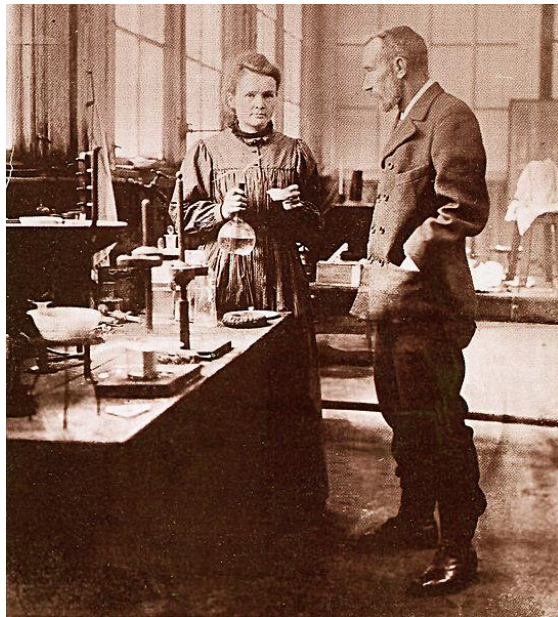
- $^{30}\text{P} \xrightarrow{\beta^+} ^{30}\text{Si}$

1937

- Emilio Segré and Carlo Perrier
- First artificial element: Tc



Segré



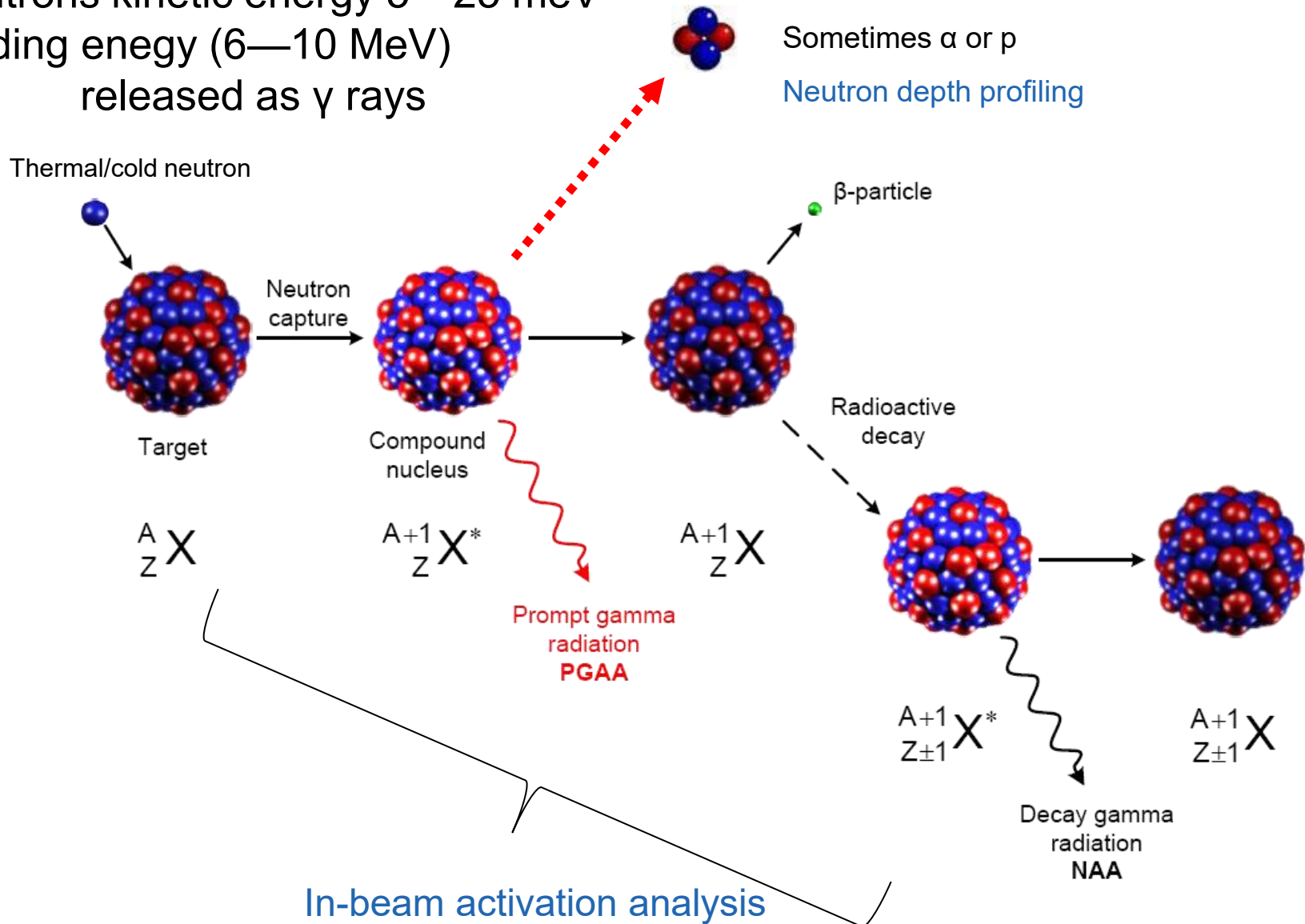
- Transformation of elements (or transmutation) needs transformation of nucleus
 - Nuclear reaction and/or
 - Radioactivity
 - Chemical separations
- A particle source to initiate the nuclear reactions
 - Nuclear reactor
 - Neutron generator
 - Spallation neutron source
 - Particle accelerator
- Separation: Nuclear chemistry lab is now a hightech, modern chemical lab with all the safety equipment



- **Charged particles, like proton, alpha (positive charge)**
 - Must be accelerated to high energies, because the nucleus is also positively charged (several MeV, meaning MV-s of accelerating voltage)
 - particles mainly ionize the target atoms
 - Useful nuclear reactions 4-6 order of magnitude less
 - We use it for production of ^{18}F (β^+ emitter, used for PET)
 - in cyclotrons: $^{18}\text{O}(p,n)^{18}\text{F}$
 - Neutron generators fusion reactions e.g. $\text{D} + \text{D} \rightarrow ^3\text{He} + \text{n}$
- Accelerated electrons also ionize the target atoms, and their interaction with the nuclei is negligible
- Photons (gamma rays) can also initiate nuclear reactions, but the probability is extremely low
- **The most efficient bombarding particle for transmutation: neutron**
 - Neutral, they can interact with the nucleus at any energy
 - High energy: $(n,2n)$, ..., inelastic scattering
 - Thermal/cold neutrons captured by nucleus
 - Cold neutrons interact with crystals as waves, neutron scattering, ...
 - Free neutrons are unstable: $\text{n} \rightarrow \text{p} + \beta^- + \bar{\nu}_e$
 - Half-life about 10 min
 - They have to be produced **freshly** (nuclear reactors, n generators, ...)



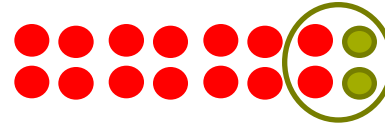
Neutrons kinetic energy 5—25 meV
Binding energy (6—10 MeV)
released as γ rays



Nucleosynthesis

- After Big Bang

- After 1 s: $n/p = 1/7$



- Free neutrons are captured $\rightarrow$ 25w% ^4He , 25ppm D (^2H), 1ppb Li (in 75w% H)

- In stars (stellar nucleosynthesis)

- Fusion reactions

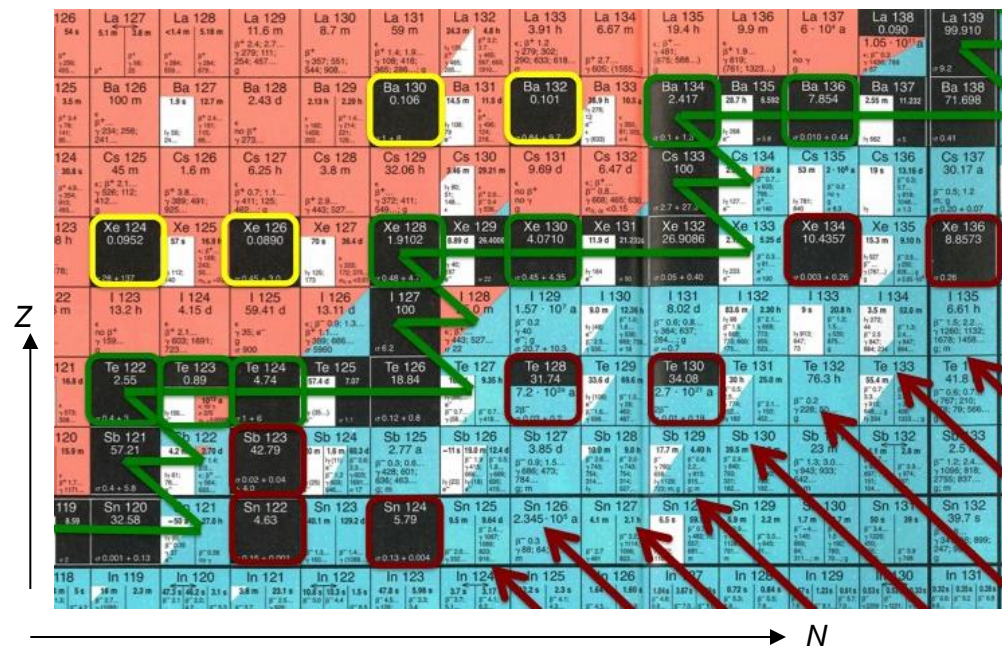
- H $\rightarrow$ He $\rightarrow$ C, N, O $\rightarrow$ Si $\rightarrow$ Fe
- Neutrons as byproduct

- Subsequent neutron captures

- Long green path through stable nuclides

- And other processes

- (Yellow, red)



Let's calculate: Neutron-induced transmutation

- Inside the reactor the flux is about $10^{14} \text{ cm}^{-2} \text{ s}^{-1}$
- When all the neutrons are absorbed and used for element production
then in a 1-cm^3 sample in a day $\sim 10^{19}$ atoms are formed
($\sim 14 \text{ }\mu\text{mol}$ in $0.1\text{--}1 \text{ mol}$) like **trace amounts**
- This is also not an efficient way of element production
- E.g. Manhattan project used reactors to produce Pu in 10 months
 - $^{238}\text{U} + n \rightarrow ^{239}\text{U} \xrightarrow{\beta^-} ^{239}\text{Np} \xrightarrow{\beta^-} ^{239}\text{Pu}$
 - 4 MW X-10 test reactor in Oak Ridge (flux $\sim 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$)
 - 250 MW production reactors in Hanford (flux $10^{13} \text{ cm}^{-2} \text{ s}^{-1}$)
 - 12 kg Pu (3×10^{25} atoms, 50 mol)
 - Critical mass for Pu is 11 kg, two bombs only **with implosion**
 - Chemical separation in Los Alamos

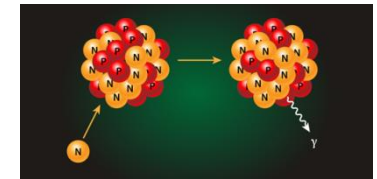
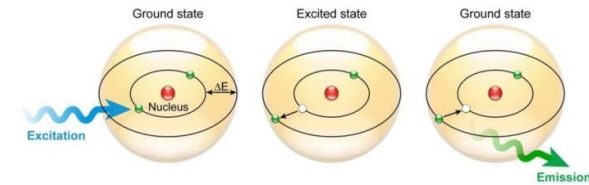


Neutron Transmutation Doping

- $^{30}\text{Si}(n,\gamma)^{31}\text{Si} \xrightarrow{\beta^-} ^{31}\text{P}$
 - ^{30}Si abundance 3%
 - ~97% of cases stable Si isotope is formed
 - ^{31}Si decays with β^- $T_{1/2} = 2.6$ h
 - Si doping plant at the FRM II RR at Garching
 - Flux $2 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$
 - Max ingot size 50 cm $\times$ Ø 20 cm (~ 16 l, 36 kg Si)
 - Irradiation length: few min – 1 day
 - Dopant concentration $4 \times 10^{12} - 3 \times 10^{14} \text{ P atom /cm}^3$ (in $5 \times 10^{22} \text{ Si atom}$),
i.e. ~ 0.1—10 ppb
 - Very homogeneous
 - FRM II can produce 15 t/year (10% of global needs)
- Gold production???: $^{196}\text{Pt}(n,\gamma)^{197}\text{Pt} \xrightarrow{\beta^-} ^{197}\text{Au}$
 - Pt \$60/g, Au \$140/g, ^{196}Pt abundance 25%

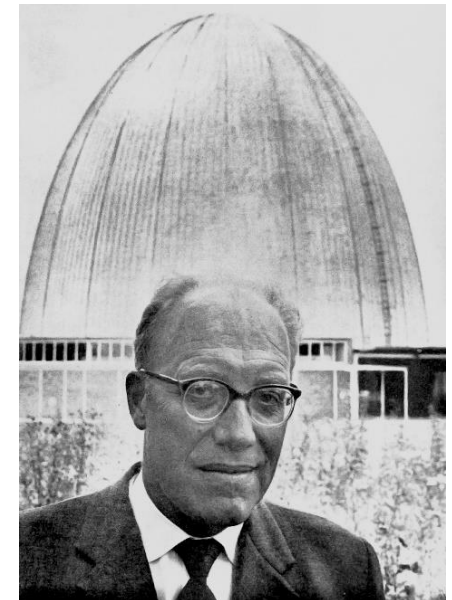


- Which elements does the samples contain in what amount?
 - 1) Excitation (bombardment); 2) deexcitation (energy release); [3) separation]
- Determination of **Z**
 - „counting” electrons
 - Exciting the electronic shell go get characterisitic radiation
 - X-rays, ... (inner shells, keVs)
 - VIS-UV (valence electrons, eVs)
 - „counting” protons
 - Exciting the nucleus to get characteristic radiation
 - Gamma rays, charged particles (**MeVs**)
- Characteristic radiation: energy identifies emitter, intensity proportional to amount
- Excitation energy ~ sensitivity
 - Higher energy, more ionization (e.g. electron-hole pairs) in the detectors
 - **Nulcear radiation 100 keV—11 MeV: very high sensitivity**
 - Transmuted atoms ~10 OoM less, than in the matrix, negligible → **non-destructive**



Discoveries/Inventions

- NAA invented by György Hevesy (Georg de Hevesy) and Hilde Levy in **1936** in Copenhagen
 - REEs with Po-Be source in paraffin
 - NAA became the most sensitive trace element analytical technique with nuclear reactors
- PGAA invented by Heinz Maier-Leibnitz in **1963** in Munich
 - H.M-L.: J. Nucl. Energy, 17 (1963) 217
 - Henkelmann-Born: first PGAA at FRM (1969)
 - "The reduction in background by use of high-quality beam is more important for analytical purposes than is an increase in the capture rate" in Neutron Capture Gamma-Ray Spectroscopy (Ed. N. Ryde), IAEA, Vienna, 1969, p.105



Chemical (= elemental) analysis with nuclear reactions

- Characteristic radiation
- Energy identifies the emitter nuclide (i.e. the isotope of an element)
- Intensity is proportional to its quantity

$$\frac{A}{\varepsilon t} = n\Phi\sigma_{\gamma}$$

A – peak area

ε – detection efficiency

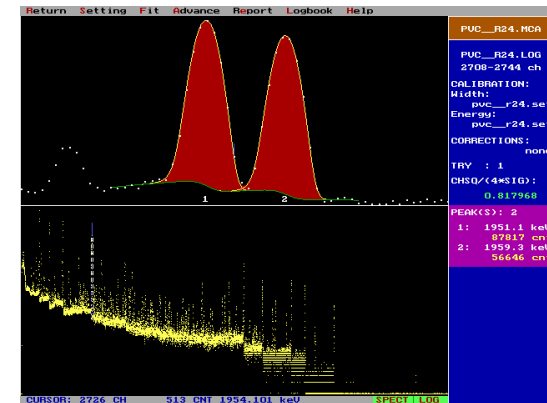
t – measurement time

n – number of atoms: $\frac{m}{M} N_A$ (mass / molar mass $\times$ Avogadro constant)

Φ – neutron flux

σ_{γ} -- partial gamma-ray production cross section: $\theta \sigma_0 P_{\gamma}$

isotopic abundance $\times$ neutron capture cross section $\times$ emission probability



Light nuclides follow $1/v$ law

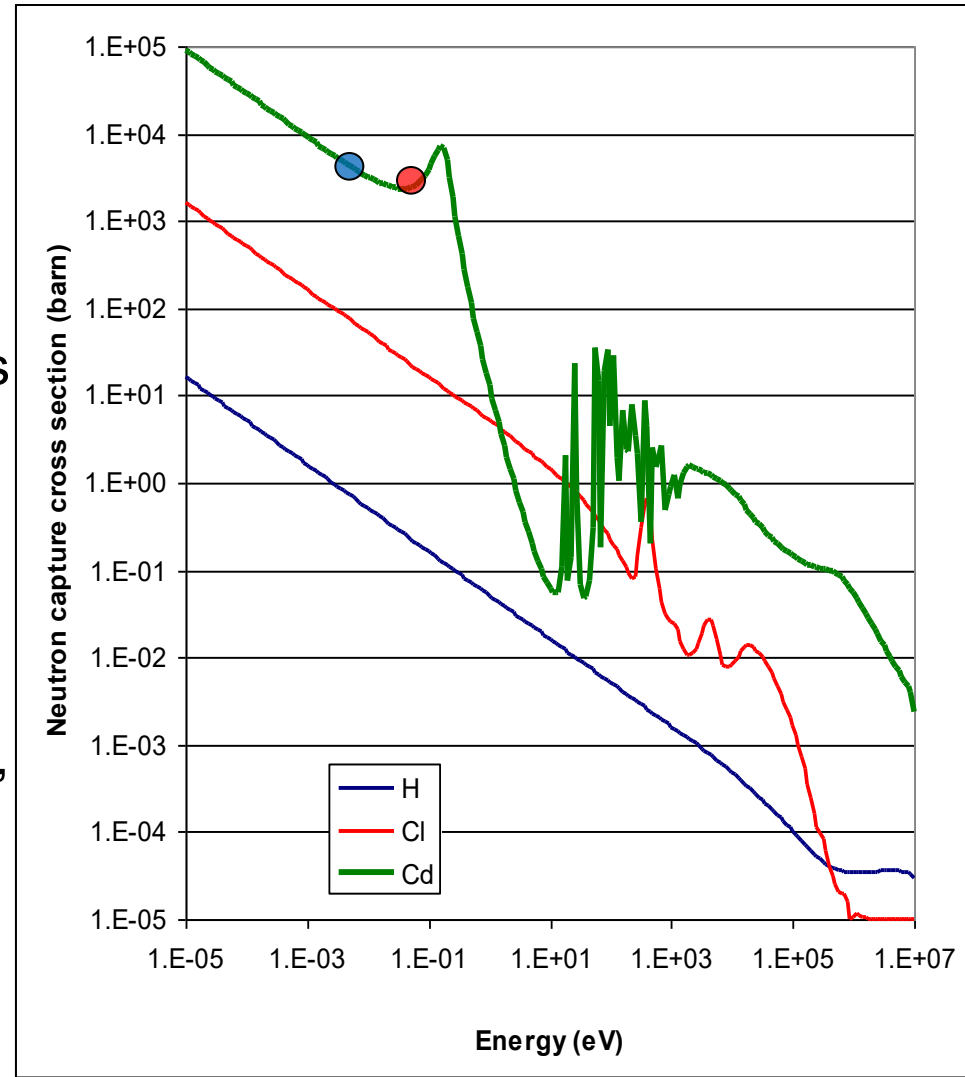
- $A > 100$ non- $1/v$ already in thermal
- In cold beam all nuclides are regular

Non- $1/v$ behaviour due to resonances

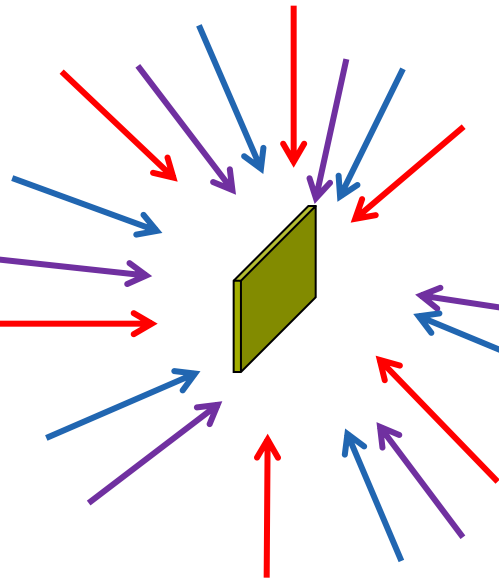
- cold beam: all nuclides regular
- thermal beam: in some cases resonances (Cd, Sm,...)

We calculate with thermal cross secs,
thus the flux will be higher in cold
beam ($\sim 4\times$)

Thermal equivalent neutron flux (Φ_0)



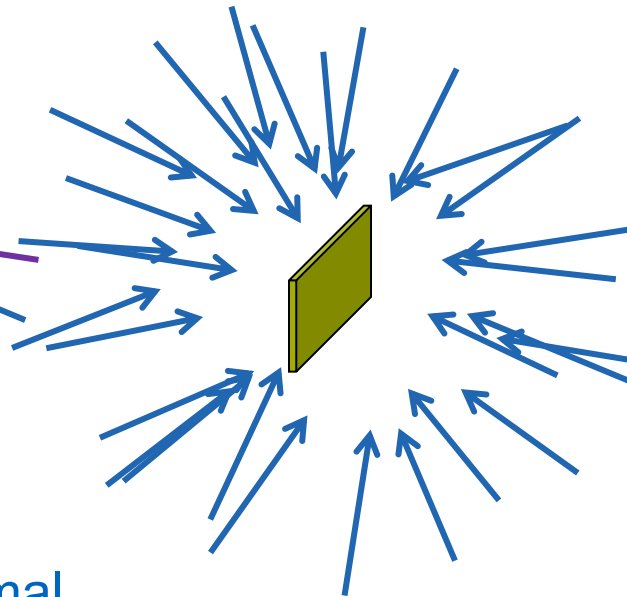
Other reactor



Thermal
Epithermal neutrons
Fast

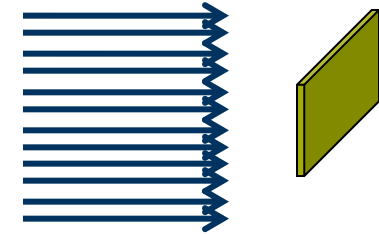
All have different attenuations

FRM2 reactor



Attenuation is easy to calculate

In beam



Only ~parallel **cold** neutrons

Probability for the emission of a given-energy gamma photon after neutron capture

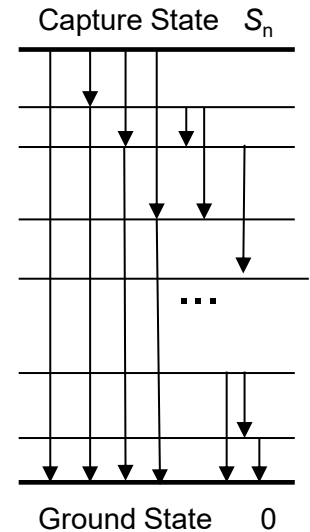
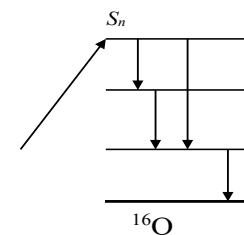
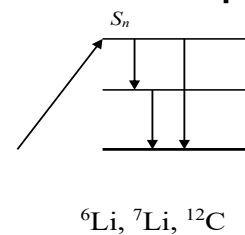
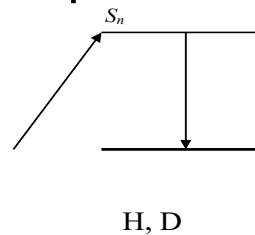
- Partial gamma-ray production cross section: σ_γ

$$\sigma_\gamma = P_\gamma \theta \sigma$$

(emission probability $\times$ isotopic abundance $\times$ capture cross-section)

Relative intensities are always the same

P_γ :



θ :

PGAA

$(\sigma_\gamma)_{\text{max}}$

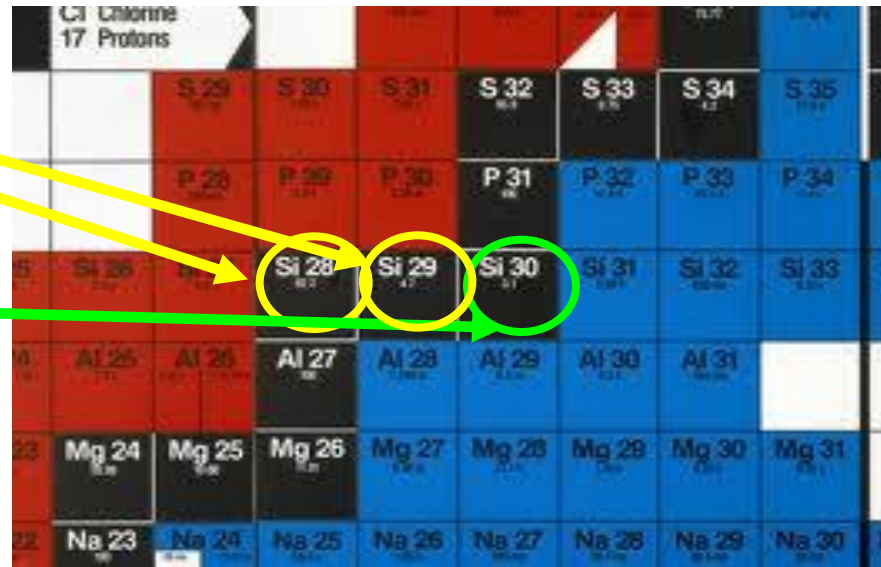
NAA

$(\sigma_\gamma)_{\text{last}}$

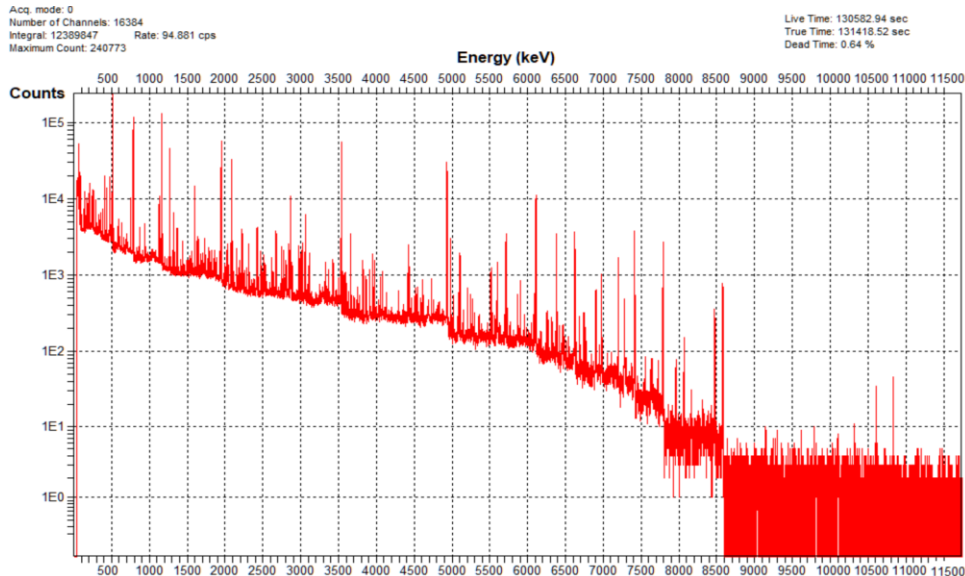
(Not always the last)

$(\sigma_\gamma)_{\text{last}} < (\sigma_\gamma)_{\text{max}}$

(~order of magnitude)

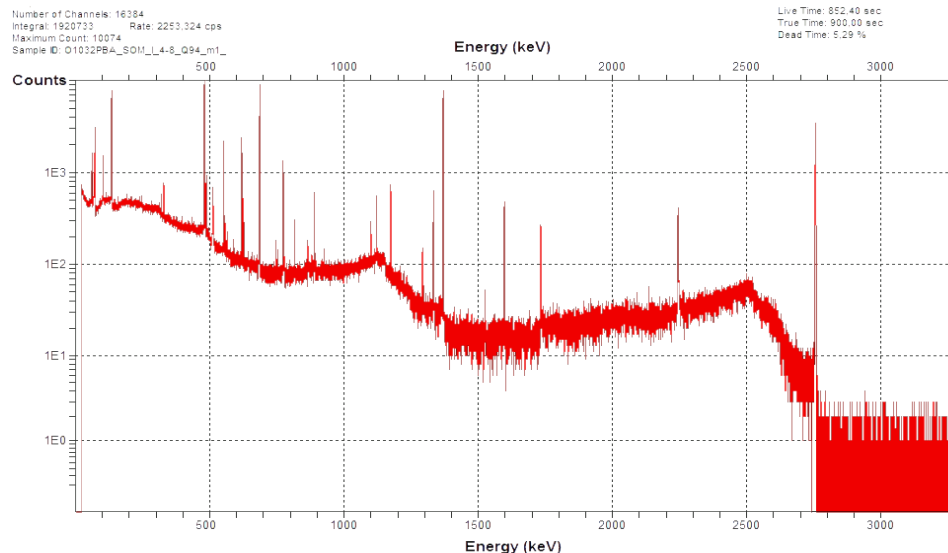


N



PGAA

- Gamma energy range up to ~12 MeV
- Complicated spectrum with up to 1000 peaks
- Peak positions -> identifying the elements
- Peak areas-> determining quantities

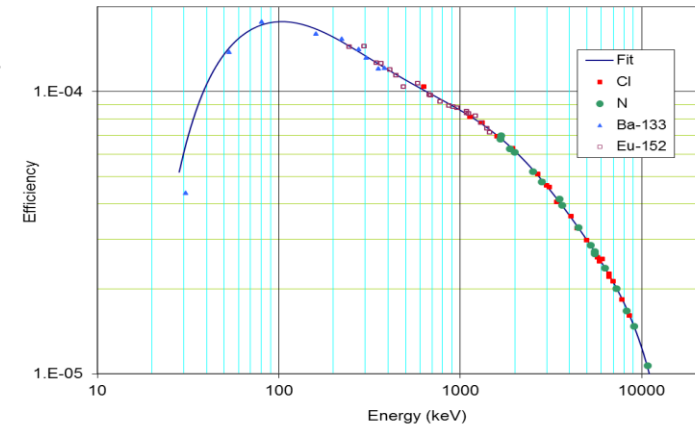


NAA

- Gamma energy range up to ~2 MeV
- Spectrum with a few dozens of peaks
- Peak positions -> identifying the elements
- Peak areas, half lives -> determining quantities

1) Efficiency

fitted with orthonormal polynomials
normalized together:
radioactive sources
(n, γ) reaction



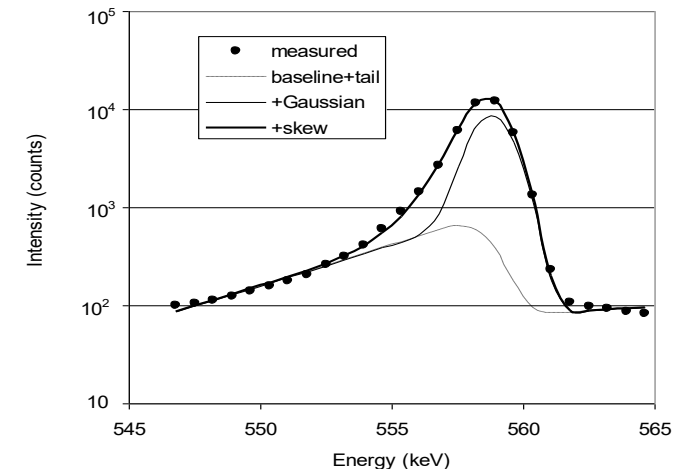
2) Energy (using calibration sources)

+ Non-linearity (similar to eff.)

3) Peak-width calibration

4) Peak-shape calibration (asymmetric parts)

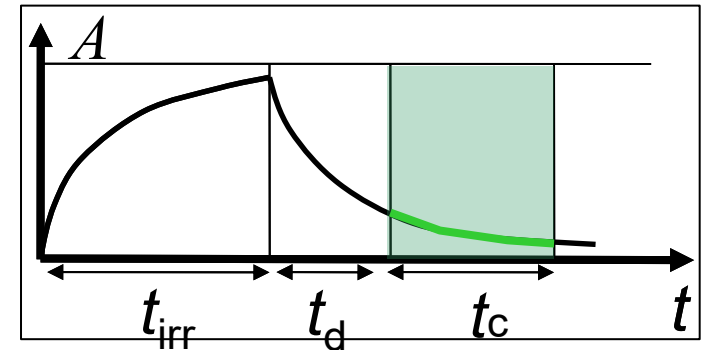
5) Backgrounds (room, beam-on, etc.)



Time dynamics in NAA and PGAA

In NAA

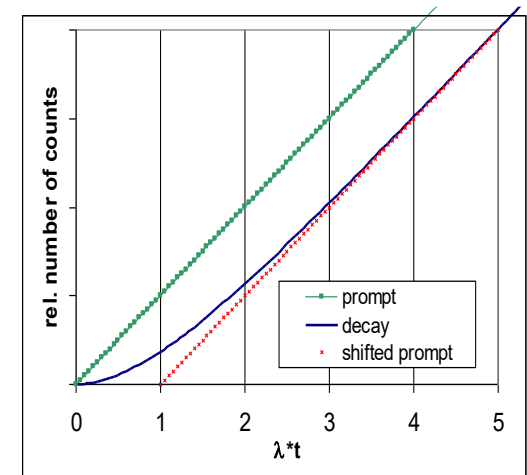
$$S = 1 - e^{-\lambda t_{irr}} \quad D = e^{-\lambda t_d} \quad C = \frac{1 - e^{-\lambda t_c}}{\lambda t_c}$$



In PGAA typically no decay correction

- If yes, in-beam decay correction factor:
 - Any systematic error from that is negligible

$$B = 1 - \frac{1 - e^{-\lambda t}}{\lambda t}$$

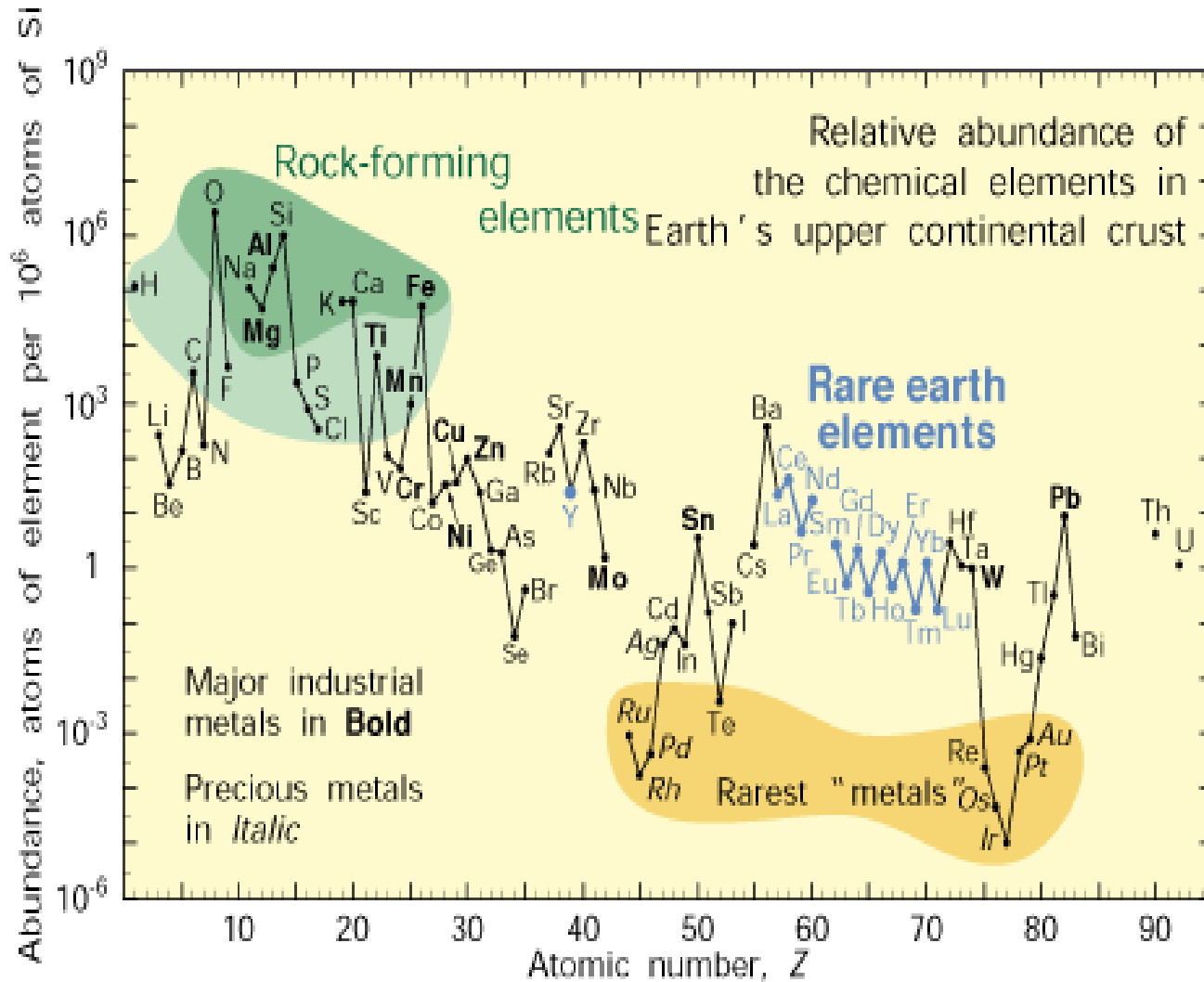


flux: $\sim 10^8 \text{ cm}^{-2} \text{ s}^{-1}$, sample mass $\sim 300\text{mg}$



Sensitivity of INAA (typical geological material)

NAA																		DL				
H																	He					
Li	Be															B	C	N	O	F	Ne	1.E-12
Na	Mg															Al	Si	P	S	Cl	Ar	1.E-10
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	1.E-08				
Rb	Sr	Y	Zr	Nb	Mo	(Tc)	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	1.E-06				
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi				1.E-04				
																		1.E-02				
																		N/D				
																		g				



- PGAA

- Light elements (H)
- Matrix constituents
 - Certain trace elements (B, Cd, REE)

- NAA

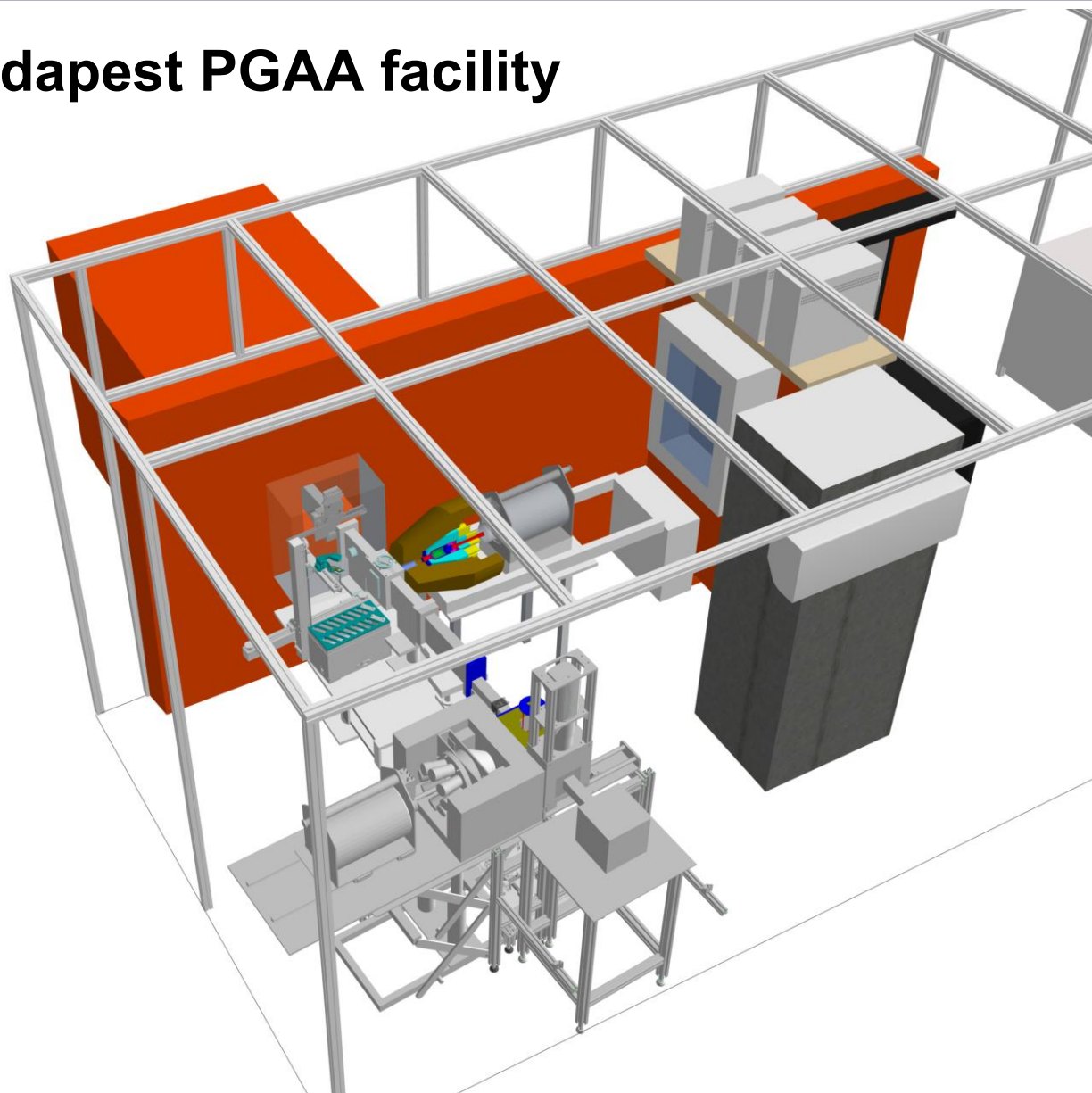
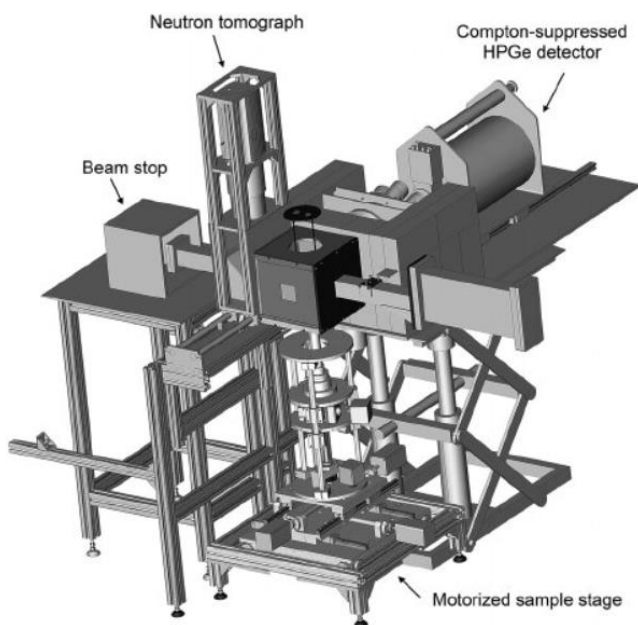
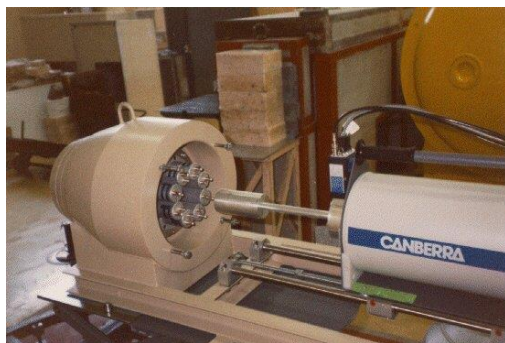
- $Z > 10$
- Really good $Z > 20$
- Trace elements

- Complete analysis

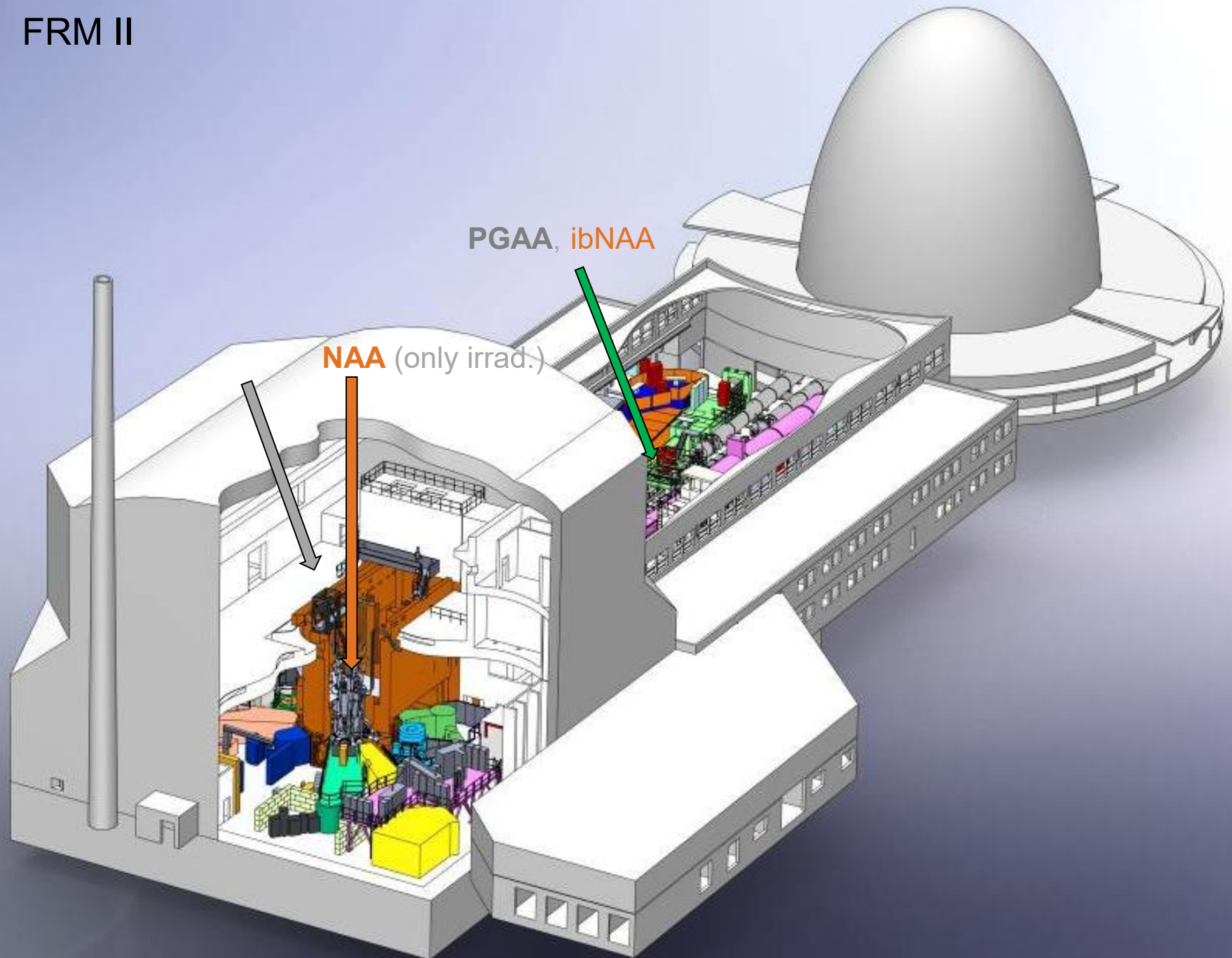
- Major components
- Minor components
- Trace elements

Budapest PGAA facility

Flux $1.5 \times 10^8 \text{ cm}^{-2} \text{ s}^{-1}$

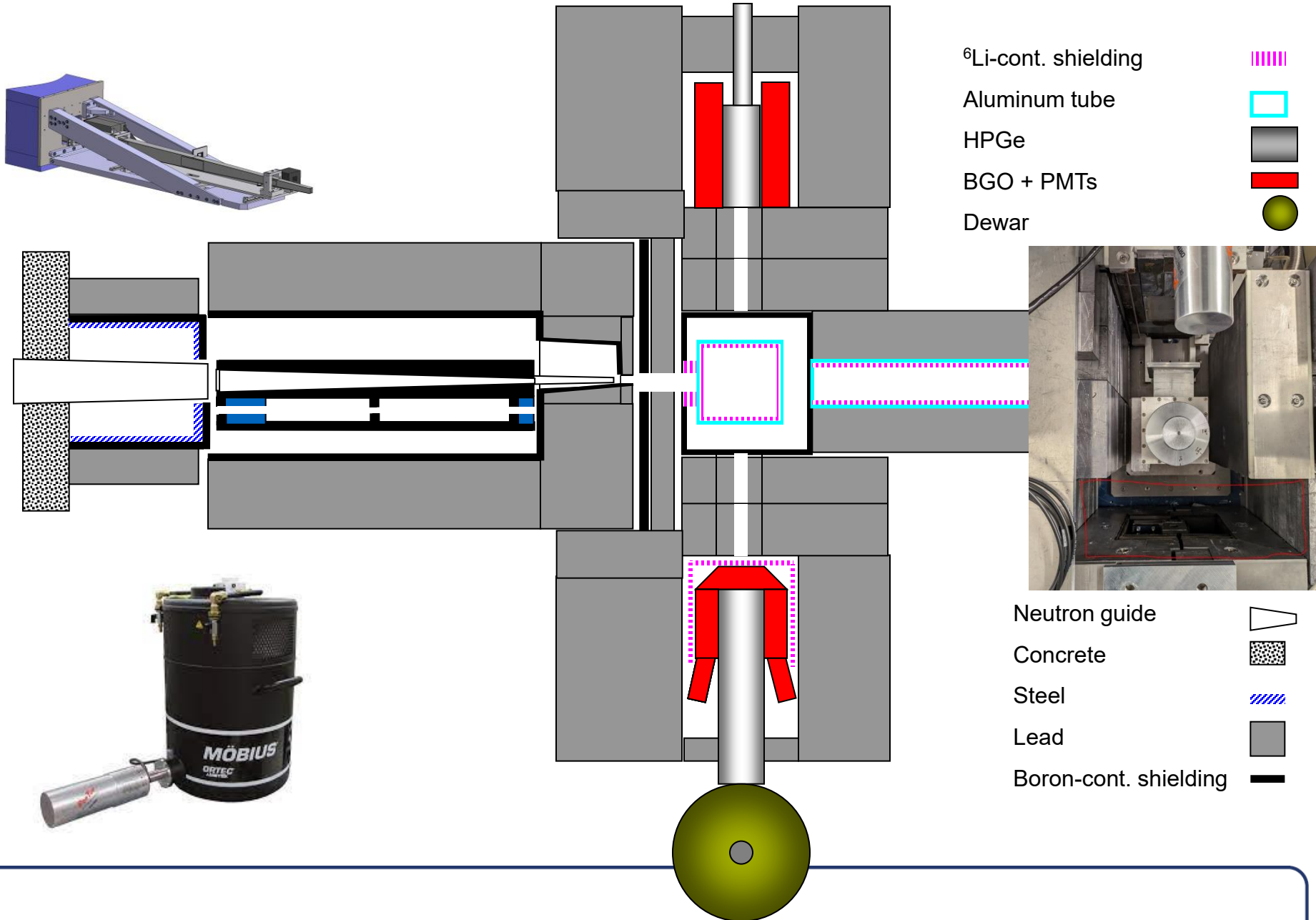


FRM II



PGAA facility at the neutron guide hall of FRM II reactor





Flux: $10^7 - 4 \times 10^{10} \text{ cm}^{-2} \text{ s}^{-1}$, HPGe with Compton suppression

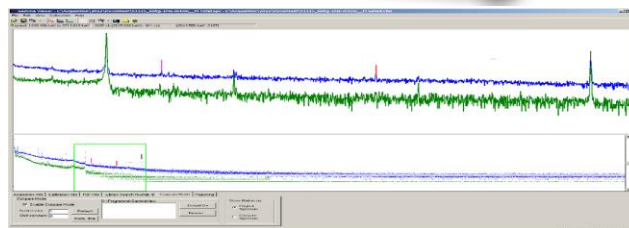
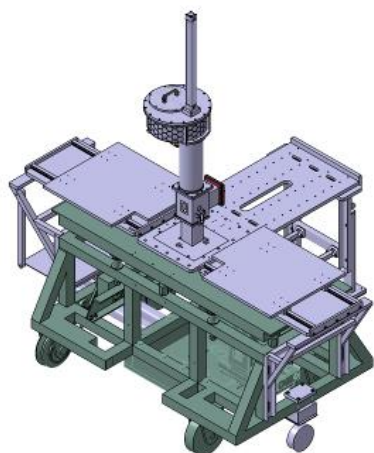
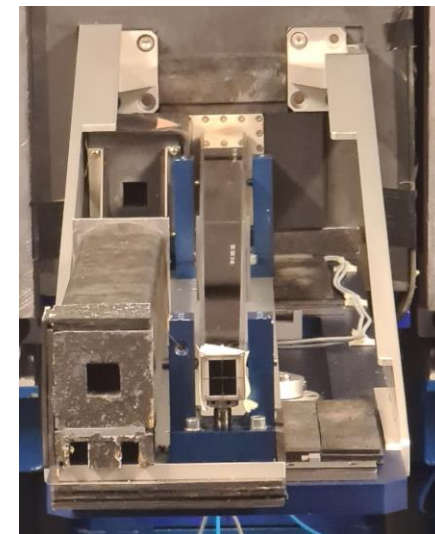
PGAA

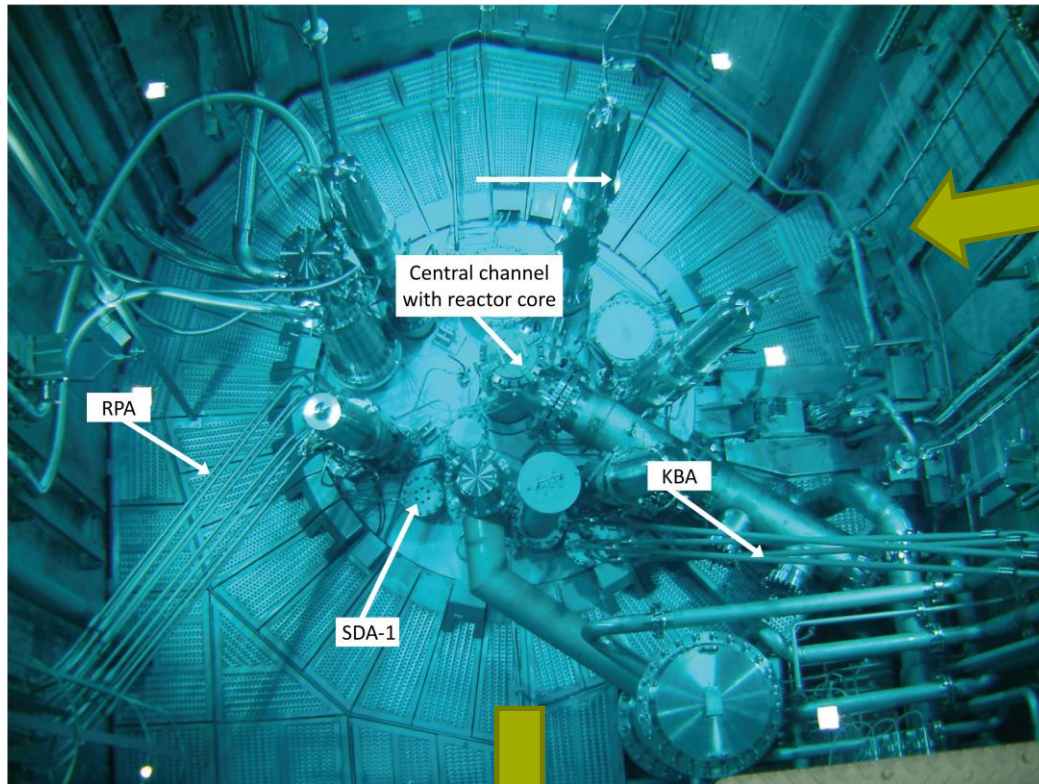


low-bkg chamber



focusing guide





FRM II:
Flux for NAA
up to $\sim 10^{14} \text{ cm}^{-2}\text{s}^{-1}$

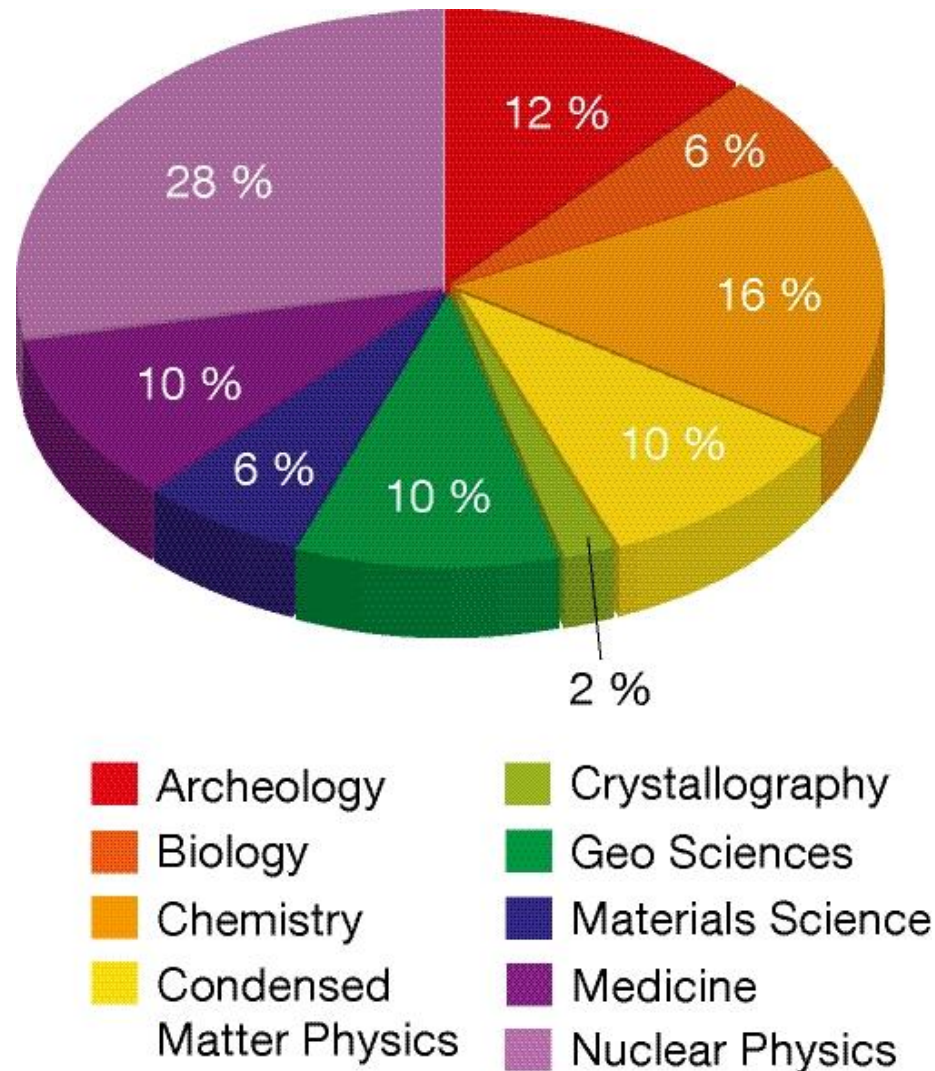


Counting stations
in the RCM

Radiochemistry Munich (RCM)

PGAA and in-beam AA

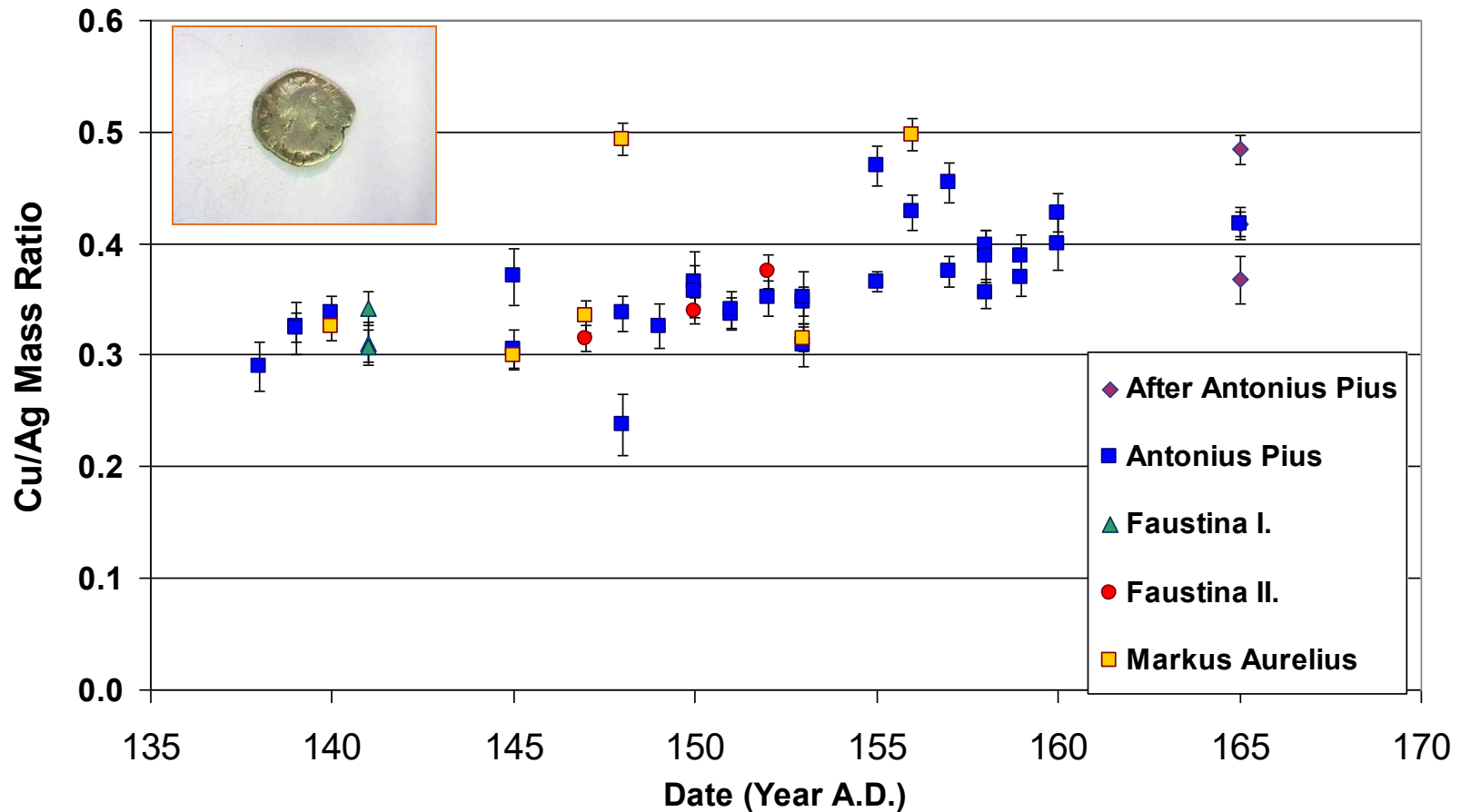
- Archeology
- D/H rate in deuterated samples
- B in different matrices
- H in different matrices
- Air filters, other environmental
- Nuclear data measurements
- Nuclear physics
- High-flux irradiation



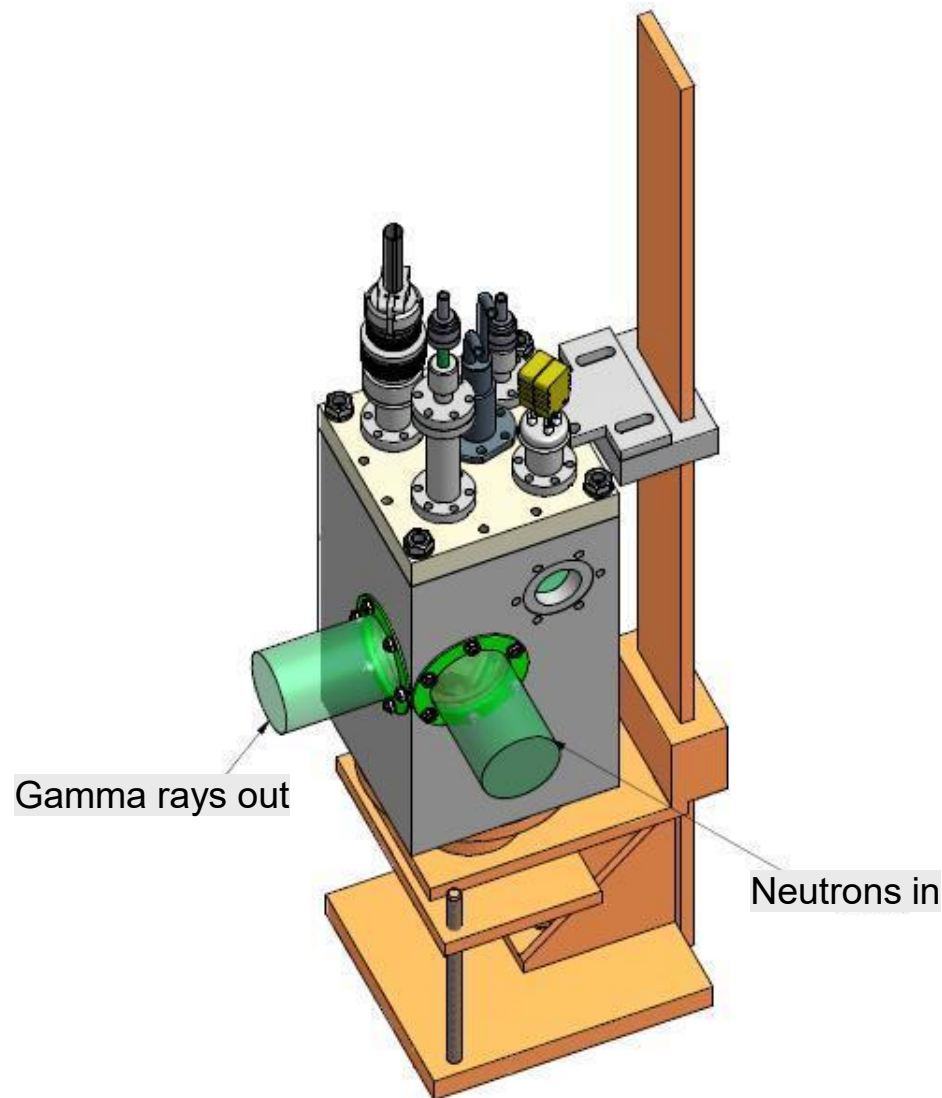
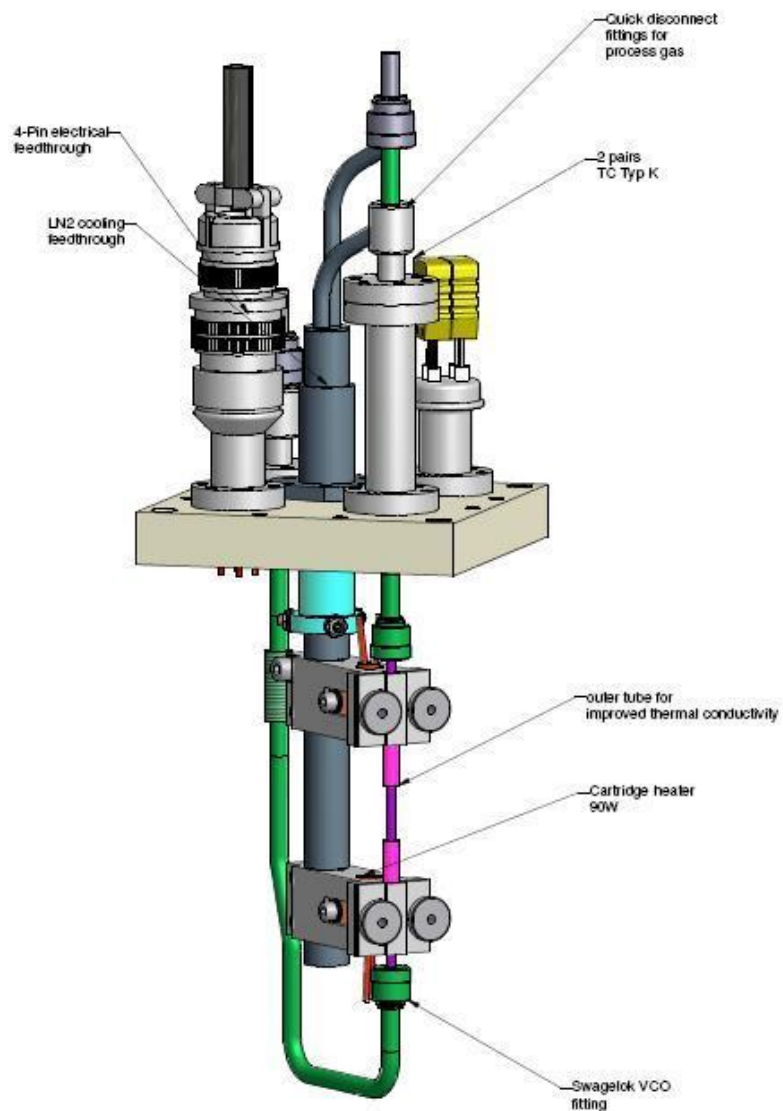
ROMAN SILVER COINS

(Inst. of Nuclear Chemistry and Technology, Warsaw)

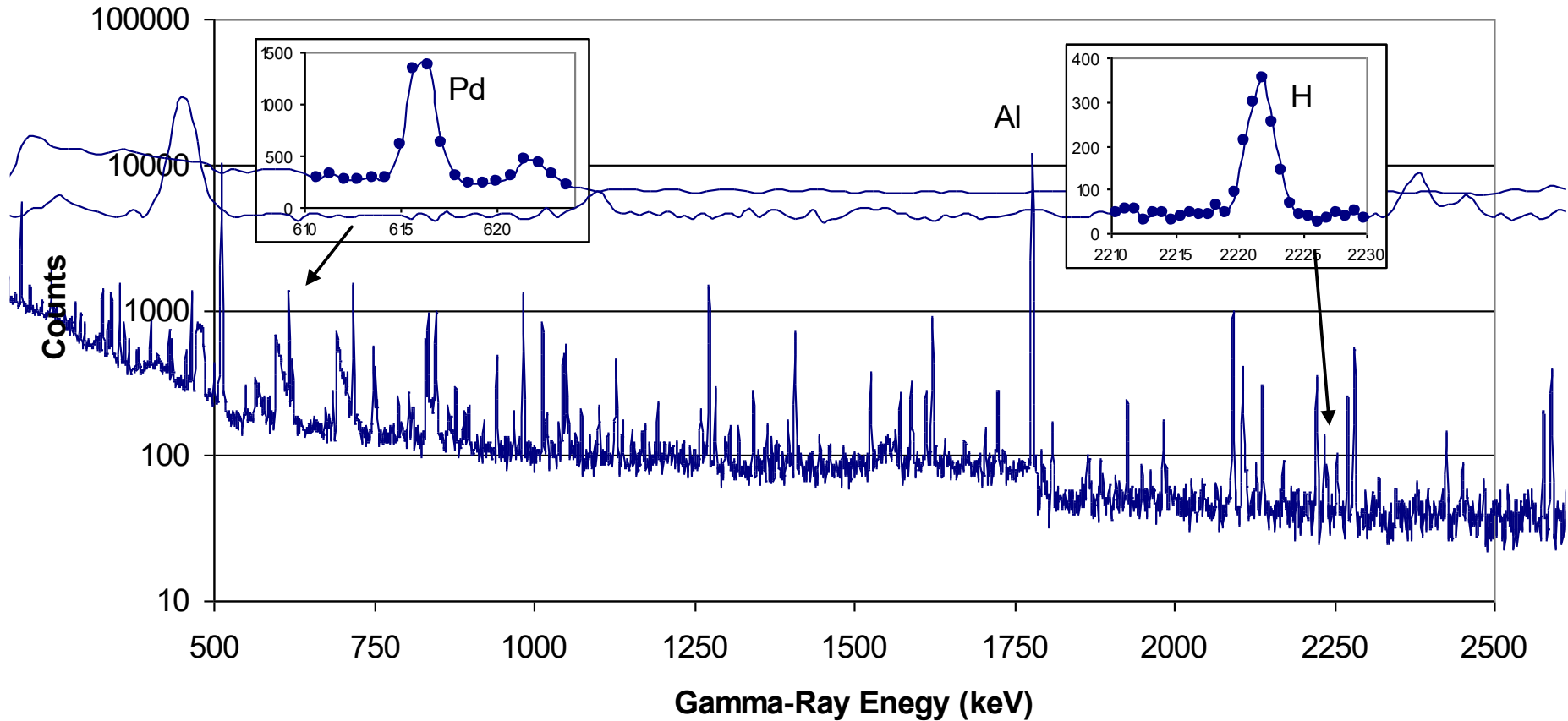
CHANGE IN COMPOSITION OF ROMAN SILVER COINS



Cathalytic cell for in situ PGAA



PGAA spectrum of cathalytic reactor



H detection limit: 5 μg !!

Analysis of Deep Sea Vents (w%)

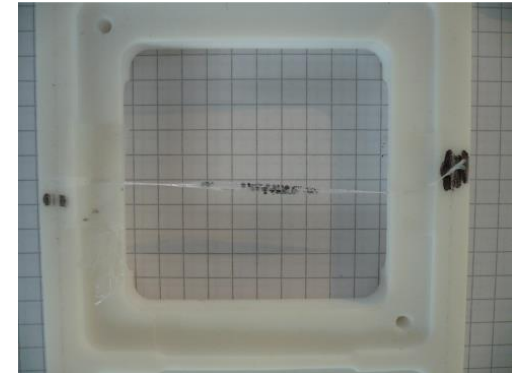
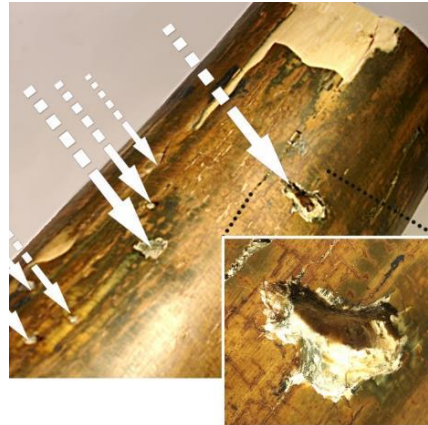
25 elements



	ALVIN 917-R4	ALVIN 1457-1R-C	ALVIN 1461-2R
O	45.9*	41(6), 44.9*	45.1*
S	20.0 (0.2)	0.151 (0.005)	0.16 (0.01)
Ca	11.3 (0.2)	7.22 (0.11)	7.25 (0.13)
Fe	9.28 (0.11)	9.65 (0.08)	9.37 (0.09)
Cu	7.67 (0.07)	---	---
Al	---	7.10 (0.07)	7.06 (0.12)
Mg	1.8 (0.2)	3.98 (0.11)	3.6 (0.2)
Zn	1.36 (0.05)	---	---
P	---	0.85 (0.18)	1.6 (0.2)
Ni	1.17 (0.003)	0.022 (0.002)	---
Ti	---	1.097 (0.008)	1.060 (0.010)
Si	0.55 (0.05)	22.6 (0.3)	22.3 (0.3)
H	0.368 (0.004)	0.0290 (0.0005)	0.027 (0.001)
K	0.27 (0.06)	0.138 (0.004)	0.16 (0.01)
Cl	0.194 (0.002)	0.0566 (0.0005)	0.0188 (0.0005)
Mn	---	0.154 (0.002)	0.161 (0.004)
Na	0.140 (0.014)	1.97 (0.04)	1.96 (0.05)
V	---	0.042 (0.002)	0.046 (0.003)
Co	0.0066 (0.0011)	0.0045 (0.0003)	0.0058 (0.0009)
Sc	---	0.0039 (0.0002)	0.0058 (0.0005)
Cd	0.00352 (0.00005)	---	0.00024 (0.00003)
B	0.00220 (0.00002)	0.000659 (0.000007)	0.000658 (0.000008)
Dy	---	0.00099 (0.00008)	0.00111 (0.00014)
Gd	0.000050 (0.000006)	0.000524 (0.000007)	0.000556 (0.000010)
Sm	0.00033 (0.00003)	0.000330 (0.000005)	0.000340 (0.000007)

Micrometeorites from mammoth tusks

- Megafauna extinction
~11000BC due to cosmic
event?
- ~0.3—2mg in 0.5µm Mylar foil



Z	EI	M	m meas	unc %	m Bkg	unc %	m net	ox. st.	m ox	unc %
1	H	1.008	5.47E-6	0.8	1.36E-6	1.5	4.11E-6	1	3.67E-5	1.2
5	B	10.81	6.74E-7	0.3	1.15E-8	1.0	6.63E-7	3	2.13E-6	0.3
13	Al	26.98	4.51E-5	2.2	1.96E-5	2.5	2.55E-5	3	4.82E-5	4.
14	Si	28.09	9.22E-5	2.8	1.96E-5	3.7	7.26E-5	4	1.55E-4	3.7
16	S	32.07	4.67E-6	14.		0.0	4.67E-6	6	1.17E-5	14.
17	Cl	35.45	1.09E-6	18.	1.15E-7	22.	9.71E-7	-1	9.71E-7	20.
20	Ca	40.08	2.10E-5	19.		0.0	2.10E-5	2	2.94E-5	19.
22	Ti	47.87	2.45E-4	2.6	1.40E-7	22.	2.45E-4	4	4.09E-4	2.6
24	Cr	52	4.03E-6	14.		0.0	4.03E-6	3	5.89E-6	14.
25	Mn	54.94	8.75E-6	2.0		0.0	8.75E-6	3	1.26E-5	2.0
26	Fe	55.85	2.31E-4	2.4	1.16E-6	10.	2.30E-4	3	3.28E-4	2.4
27	Co	58.93	3.06E-6	3.1		0.0	3.06E-6	2	3.89E-6	3.1
60	Nd	144.2	8.89E-7	13.		0.0	8.89E-7	3	1.04E-6	13.
62	Sm	150.4	5.32E-8	6.		0.0	5.32E-8	3	6.16E-8	6.
64	Gd	157.3	9.89E-8	7.		0.0	9.89E-8	3	1.14E-7	7.

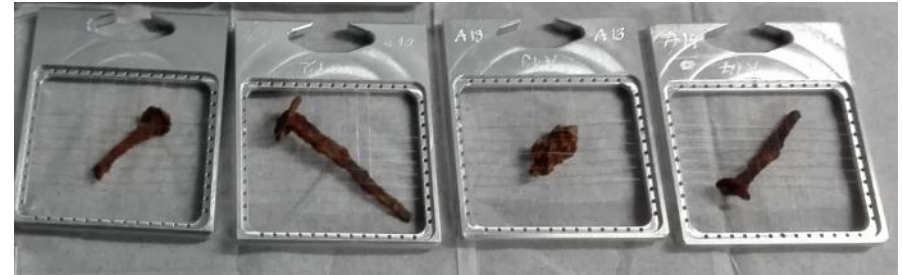


Total: ~1 mg

R.B. Firestone

Archaeometry

- Chlorine in iron objects
 - Slow down the corrosion of artifacts
 - Understand the corrosion of iron
- Carbonate layers in aqueducts
 - Trace elements
 - Hydrologic history



Lichen checking air pollution

Z	El	M	m meas	unc %	m Bkg	unc %	m net	ox. st.	m ox	unc %	mol%	unc %	w% el/el	unc %
1	H	1.008	1.18E-2	0.4	2.44E-7	1.7	1.18E-2	1	0.11	0.4	48.6	2.2	6.17	4.
5	B	10.81	1.14E-6	0.4	3.87E-9	0.9	1.13E-6	3	3.65E-6	0.4	4.35 ppm	2.2	5.92 ppm	4.
6	C	12.01	0.107	3.1	3.50E-2	3.0	0.07	4	0.26	5.	25	4.	38	5.
7	N	14.01	2.32E-3	2.1		0.0	2.32E-3	5	8.95E-3	2.1	0.69	3.0	1.21	5.
13	Al	26.98	7.32E-4	2.1	1.38E-4	2.0	5.93E-4	3	1.12E-3	2.6	0.091	3.4	0.31	5.
14	Si	28.09	1.85E-3	3.1		0.0	1.85E-3	4	3.95E-3	3.1	0.27	3.7	0.97	5.
16	S	32.07	2.47E-4	2.6		0.0	2.47E-4	6	6.17E-4	2.6	320 ppm	3.3	0.129	5.
17	Cl	35.45	9.91E-5	1.7	9.27E-8	2.4	9.90E-5	-1	9.90E-5	1.7	116 ppm	2.7	0.052	4.
19	K	39.1	9.92E-4	1.7		0.0	9.92E-4	1	1.20E-3	1.7	0.105	2.7	0.52	4.
22	Ti	47.87	3.50E-5	3.0		0.0	3.50E-5	4	5.84E-5	3.0	30 ppm	3.7	180 ppm	5.
25	Mn	54.94	5.05E-6	7.		0.0	5.05E-6	3	7.25E-6	7.	3.8 ppm	8.	26 ppm	9.
48	Cd	112.4	3.06E-8	4.0		0.0	3.06E-8	2	3.49E-8	4.0	0.0113ppm	5.	0.16 ppm	6.
62	Sm	150.4	3.73E-8	2.8		0.0	3.73E-8	3	4.33E-8	2.8	0.0103ppm	3.5	0.19 ppm	5.
64	Gd	157.3	4.45E-8	6.		0.0	4.45E-8	3	5.13E-8	6.	0.012ppm	6.	0.23 ppm	7.
		0												
8	O	16	0.096	7.		0.0	0.10	-2		7.	25	6.	50	4.
		0												
11	Na	22.99	5.22E-5	0.7		0.0	5.22E-5	1	7.03E-5	0.7	94 ppm	2.3	273 ppm	4.
17	Cl	35.45	1.02E-4	3.0		2.4	1.02E-4	-1	1.02E-4	3.0	120 ppm	3.7	0.053	5.
20	Ca	40.08	5.54E-3	13.		0.0	5.54E-3	2	7.75E-3	13.	0.6	13.	2.9	13.
21	Sc	44.96	3.36E-8	4.		0.0	3.36E-8	3	5.15E-8	4.	0.031ppm	5.	0.18 ppm	6.
23	V	50.94	6.64E-7	23.		0.0	6.64E-7	5	1.19E-6	23.	0.5 ppm	23.	3 ppm	23.
25	Mn	54.94	5.06E-6	2.2		0.0	5.06E-6	3	7.28E-6	2.2	3.8 ppm	3.1	26 ppm	5.
26	Fe	55.85	1.00E-4	15.		8.	1.00E-4	3	1.43E-4	15.	70 ppm	15.	0.05	15.
27	Co	58.93	1.25E-7	12.		0.0	1.25E-7	2	1.59E-7	12.	0.09 ppm	13.	0.7 ppm	13.
35	Br	79.9	2.00E-6	8.		0.0	2.00E-6	-1	2.00E-6	8.	1.0 ppm	9.	10 ppm	9.
38	Sr	87.62	1.09E-5	8.		0.0	1.09E-5	2	1.29E-5	8.	5.2 ppm	8.	57 ppm	9.
63	Eu	152	7.21E-9	8.		0.0	7.21E-9	3	8.35E-9	8.	0.0020ppm	9.	0.038ppm	9.
		0												



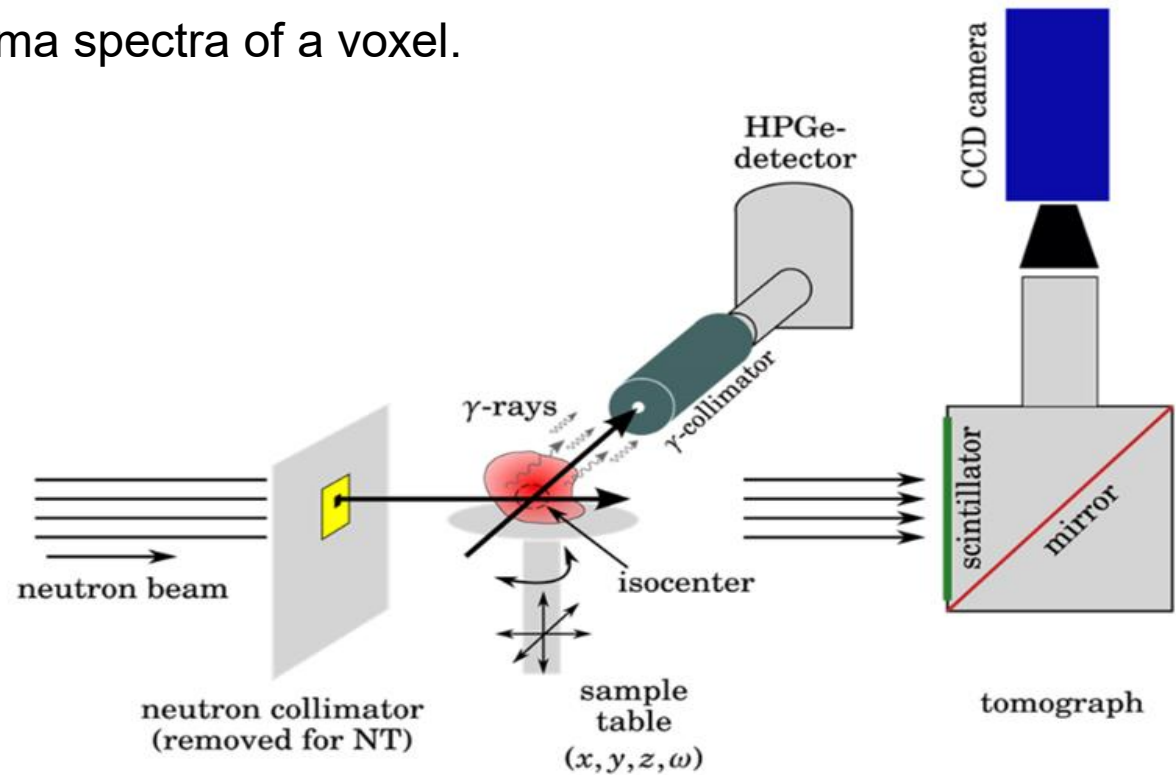
PGAA

stoichiometry



ibNAA

1. Radiography to find spots of interest.
2. Automated collimators (n and γ).
3. Acquire prompt gamma spectra of a voxel.
4. 3D elemental map



Cultural Heritage: Analysis of ancient objects

Spatially resolved prompt gamma ray activation imaging (PGA) in combination with neutron tomography (NT)

→ enables **non-destructive** view inside ancient objects

→ **element distribution** and **structure**

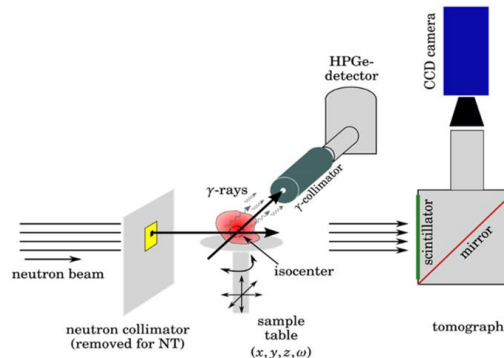
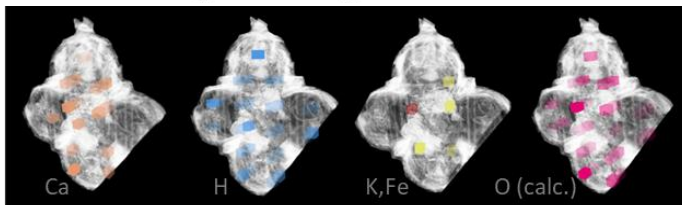


photo:
S. Steidl, RGZM



rare piece: only 3 other
phylacteries of this type
known

measurements revealed
e.g. bone material
(Ca content + structure)

Heinzel, M., Schillinger, B., Kemper, D., **Stieghorst, C.**, & Kluge, E. (2022). Discovery of a 12th-Century Enamelled Reliquary Pendant: Elemental Analysis and Content Visualisation Using Prompt Gamma Neutron Activation Analysis and Neutron Tomography. In *INTERIM MEETING OF THE ICOM-CC METALS WORKING GROUP*

Further example: Roman amulet

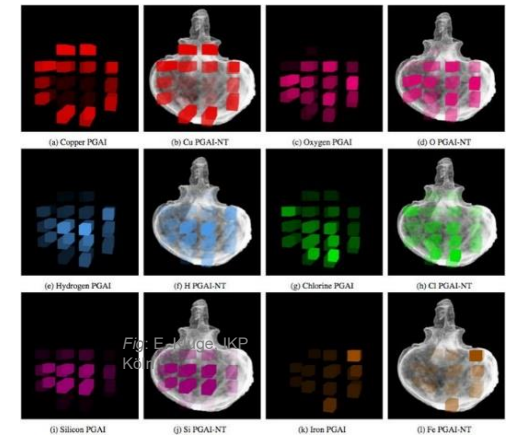
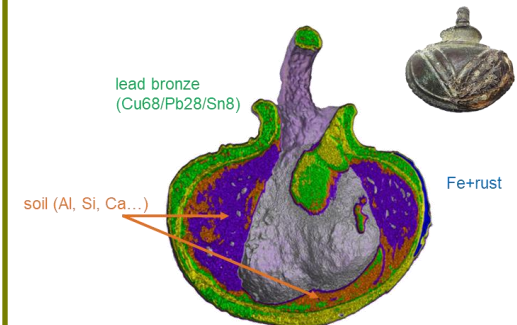


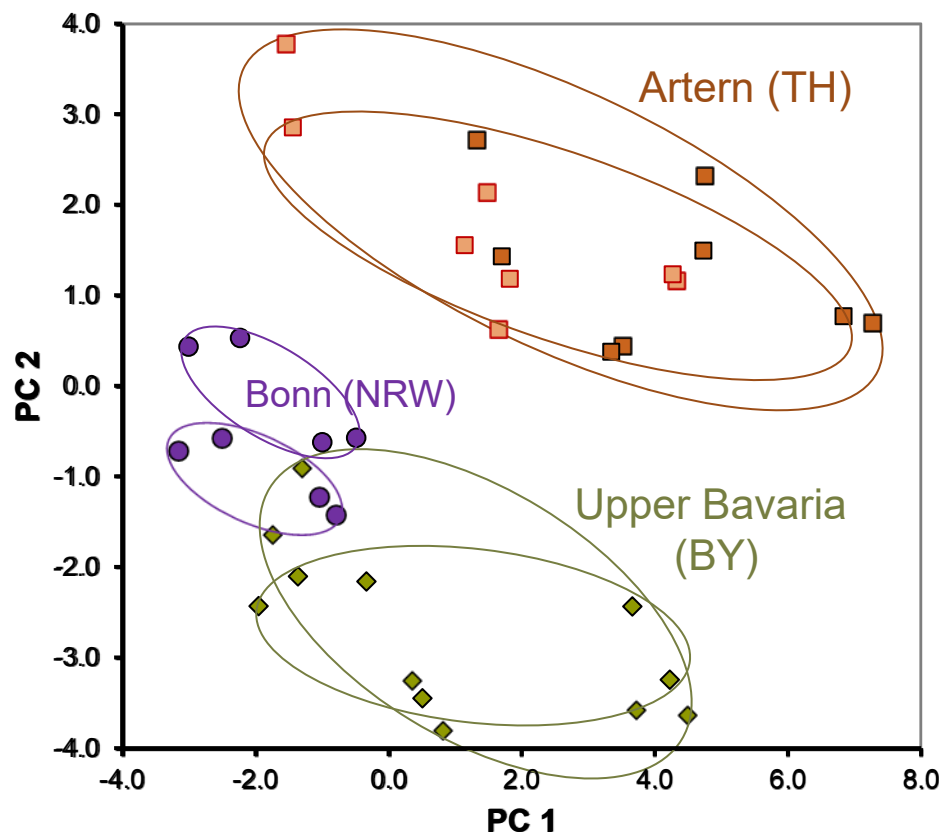
Fig. 5 Kluge, JKP
Kör



Future:

- (1) stronger linking of NT and PGA data
- (2) multi-detector approach

Element analysis of German summer truffles (*T. aestivum*)



Food Fraud Analysis

T. aestivum: up to few
100 \$/kg, *T. magnatum*:
several \$/kg

- Clustering into **groups** with respect to geographical origin
- **Statistical filter**: skewness

B, Na, Si, P, S, Cl, K, Ca; Sc, Co, Rb, Hf; Al, Cr, Cu, Mn, Ni, As, Y,
Mo, La, Nd; Fe, Zn, Cd, Ce (green = skewness > 15 %)

(4th sampling site not drawn in diagram, scattering much higher)

Rosbach, M., Stieghorst, C.,
Polkowska-Motrenko, H. et al.
J Radioanal Nucl Chem (2019)
320: 475

Thank you!