PIXE analysis of antique pottery from the Mediterranean sea area

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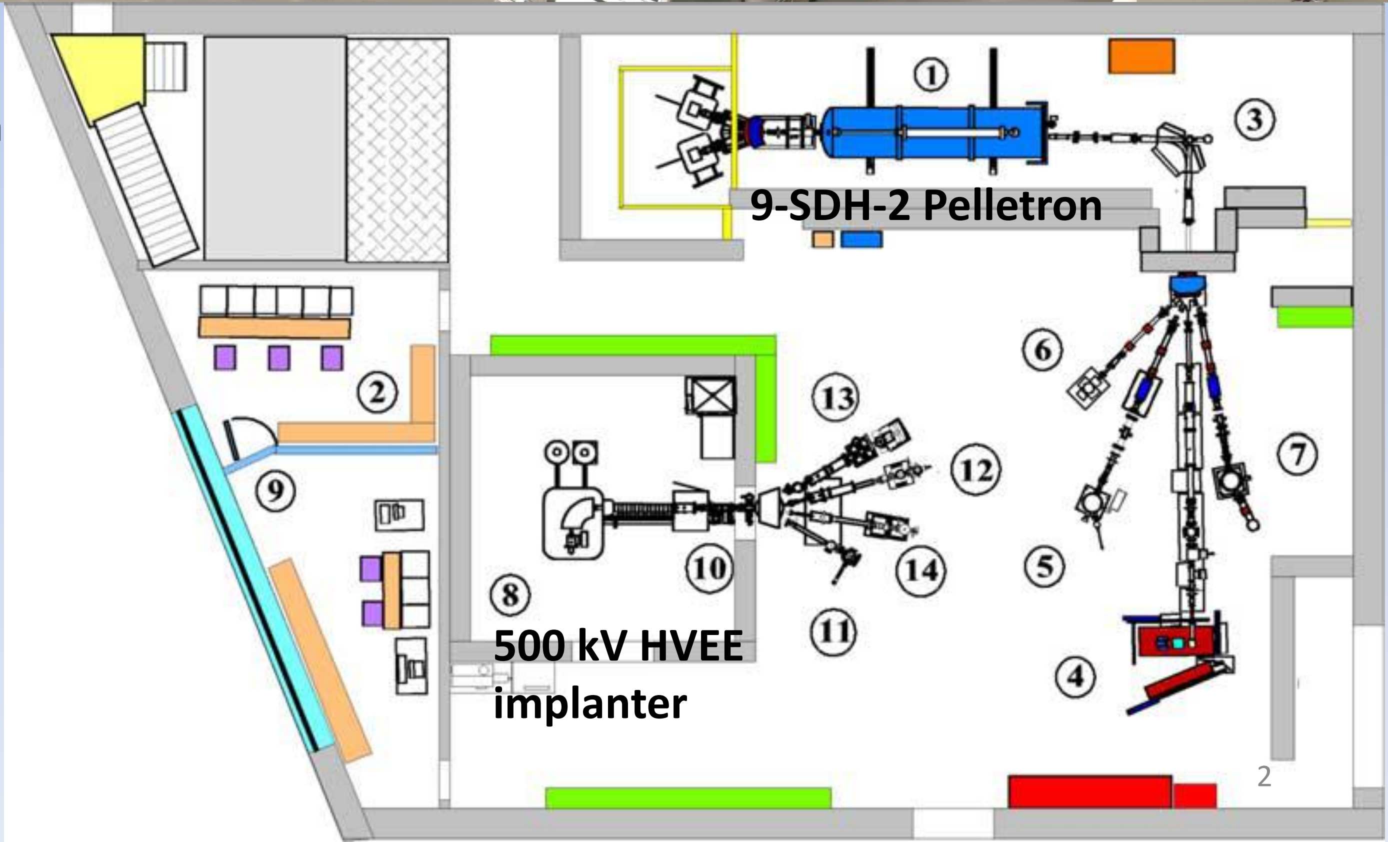
- Collecting antique pottery in Sicily (Italy)
- Analysis at the Göttingen Tandem accelerator
- Experimental setup and calibration
- Results
- Outlook

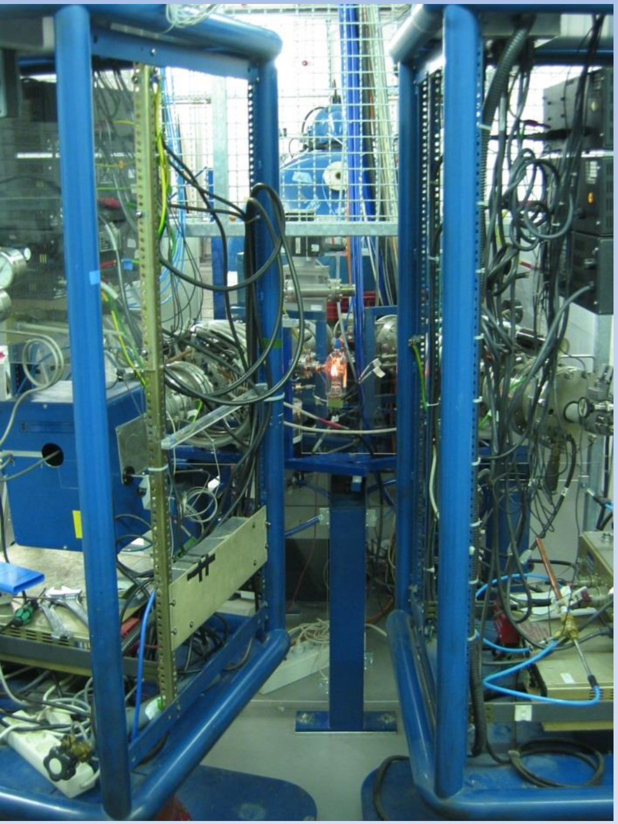
Contact : H. Hofsäss, hans.hofsaess@phys.uni-goettingen.de

6 : external proton beam
PIXE, RBS, C-ERDA
4 : NRA
5 : µ-beam
7 : Implantation
11: RBS
13: NRA
14: HR-RBS
15: Implantation



NeC 9HDS2 tandem ccelerator

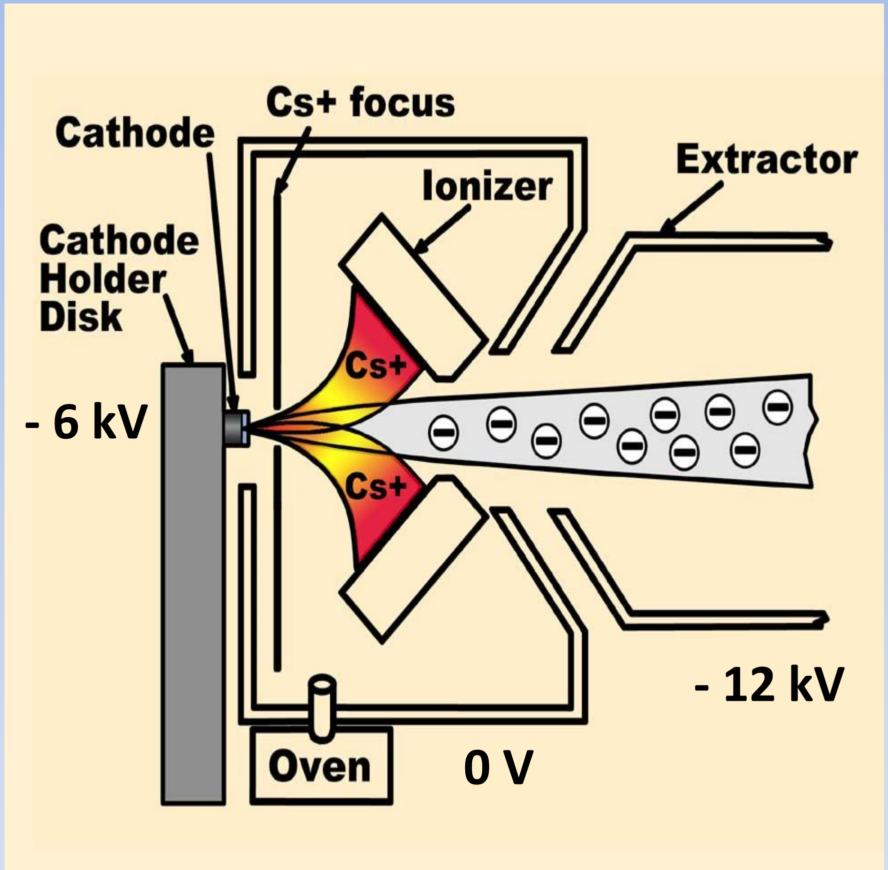
Ion sources for negative ions

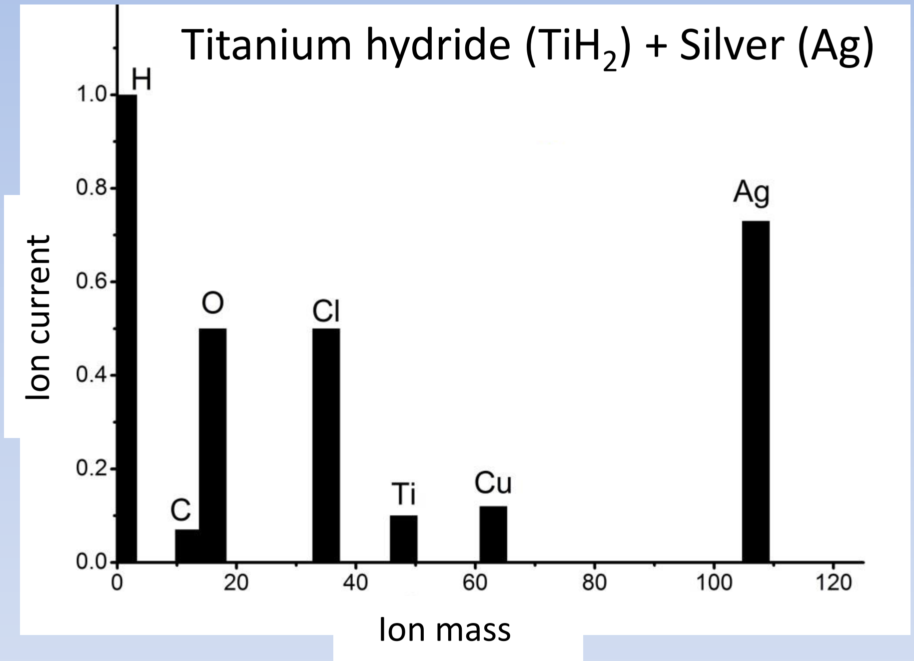


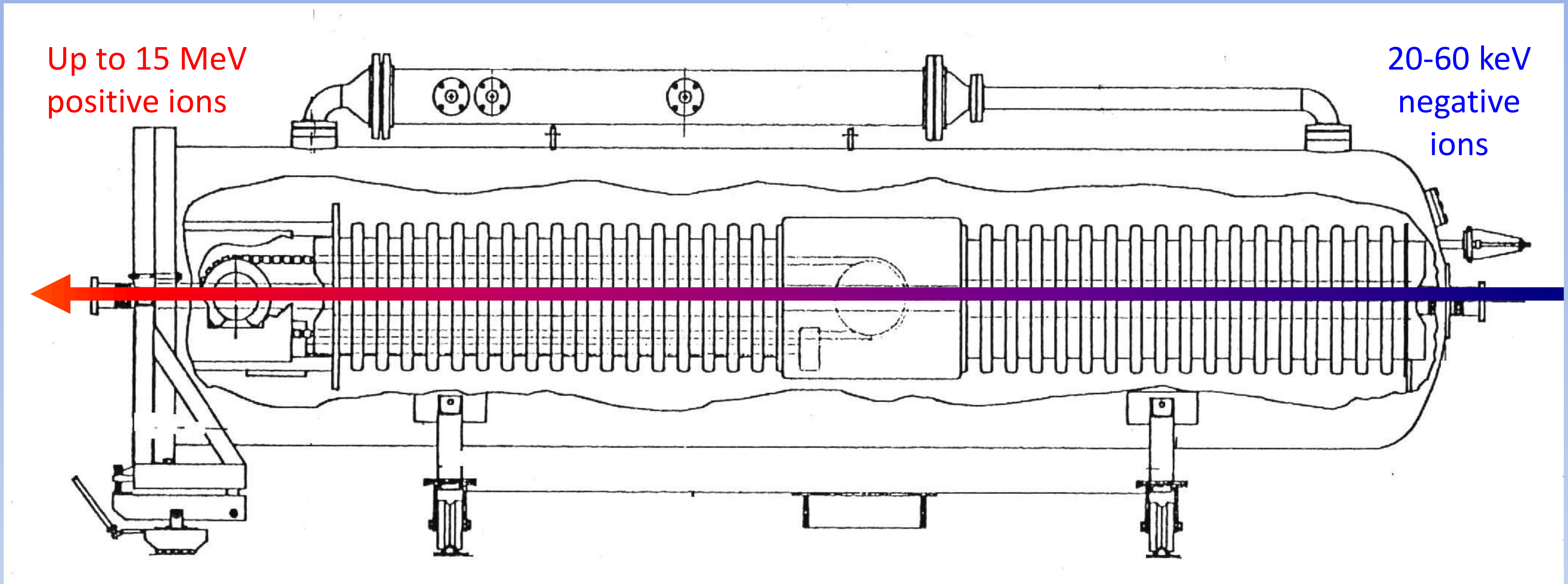
Accelerator tank filled with 3 bar SF_6

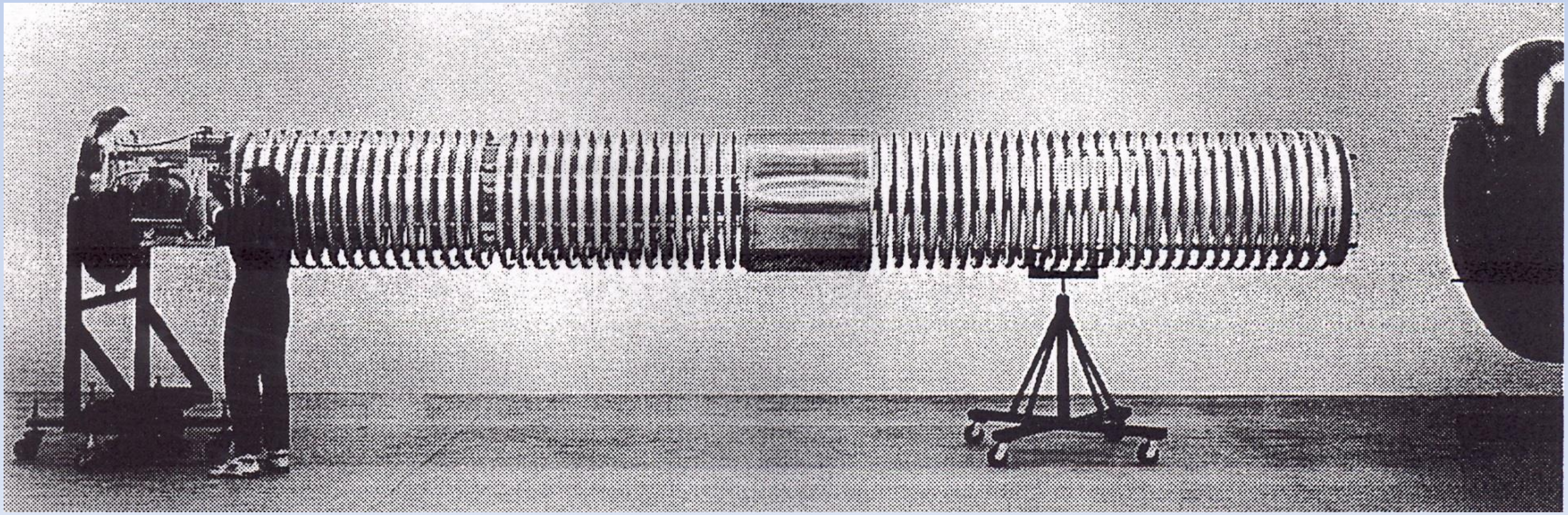
Proton micro beam line

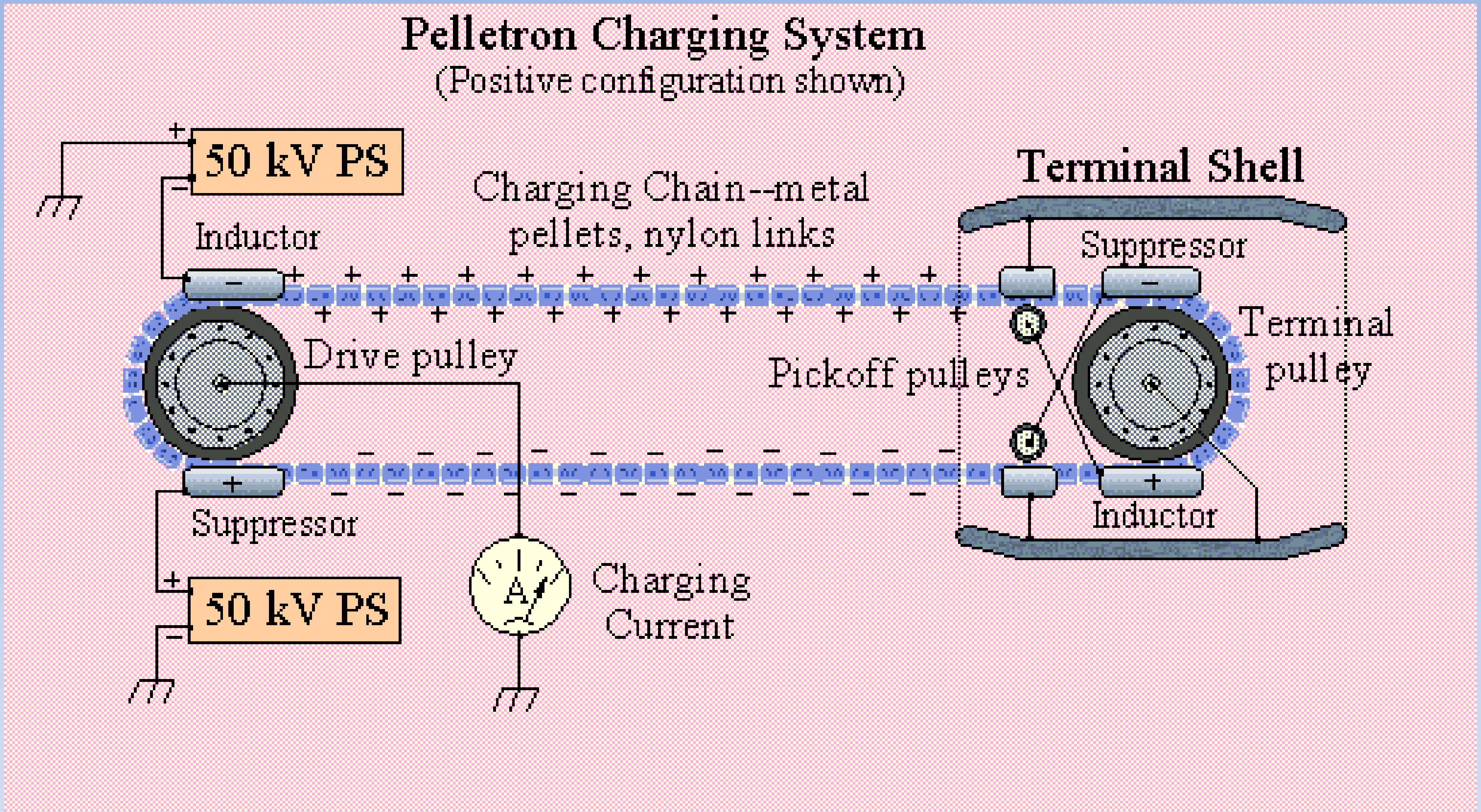
Source of negative ions by Cesium sputtering (**SNICS**)



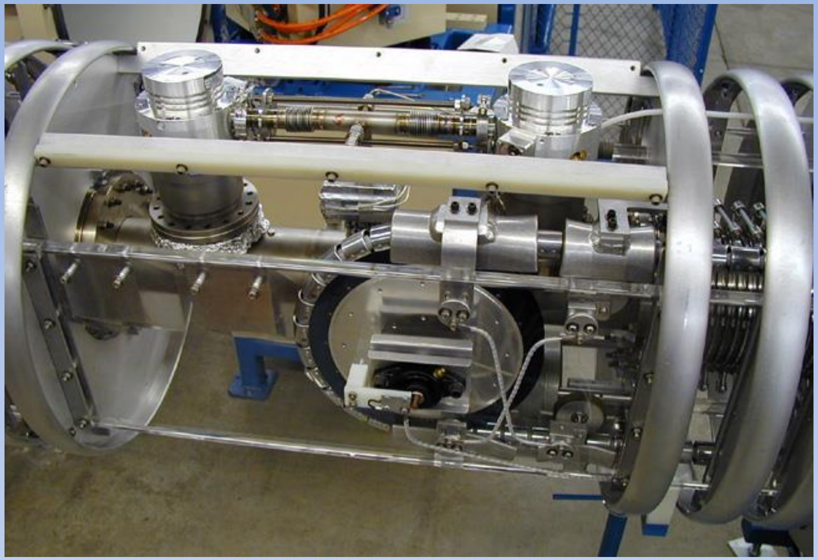


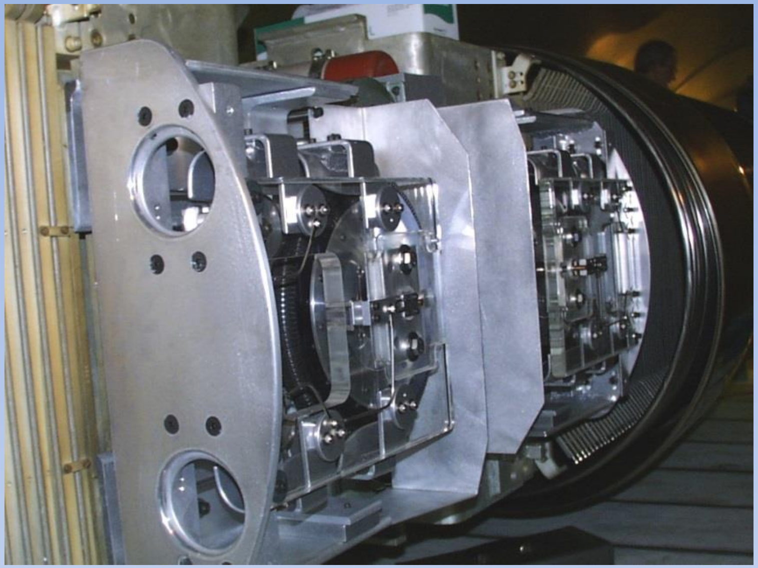

Up to 15 MeV
positive ions
20-60 keV
negative
ions

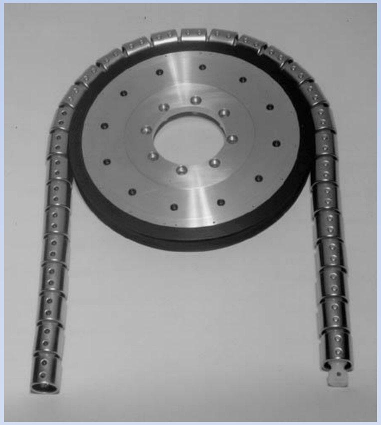




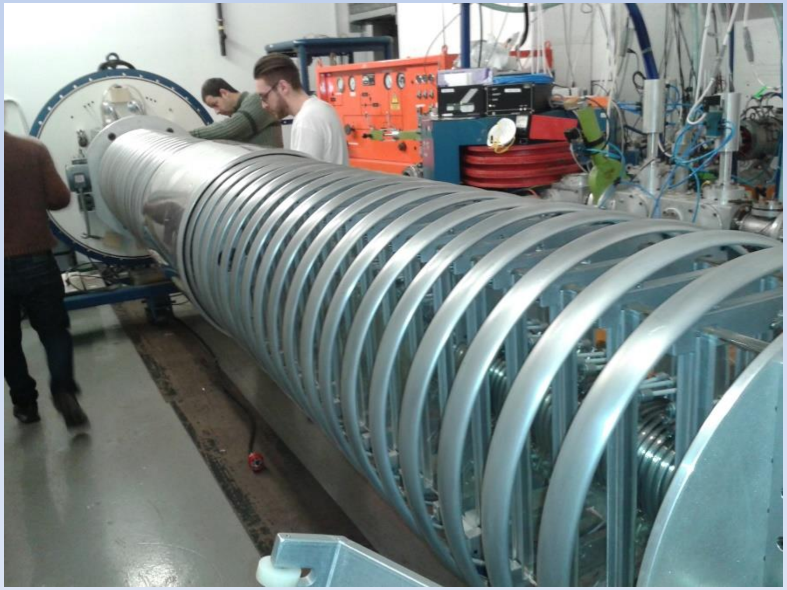
Pelletron Charging System
(Positive configuration shown)
50 kV PS
Charging Chain--metal pellets, nylon links
Terminal Shell
Inductor
Suppressor
Drive pulley
Pickoff pulleys
Terminal pulley
Suppressor
Inductor
50 kV PS
A
Charging Current







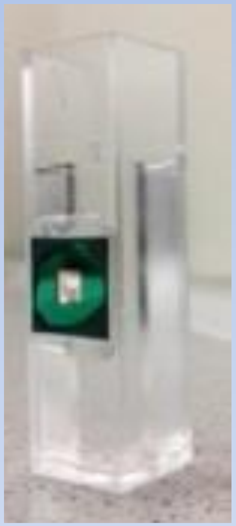
Maintenance Feb 2018

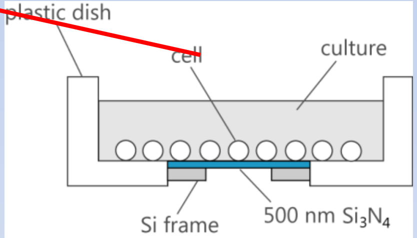


Motivation for experiments with external proton beam (protons extracted into air)

Light element analysis in samples which cannot be handled in vacuum

- Because it is easier to handle sample under ambient pressure
- Water containing samples
- Porous samples with air inclusions
- Liquid samples
- Cells – plant tissue, animal cells



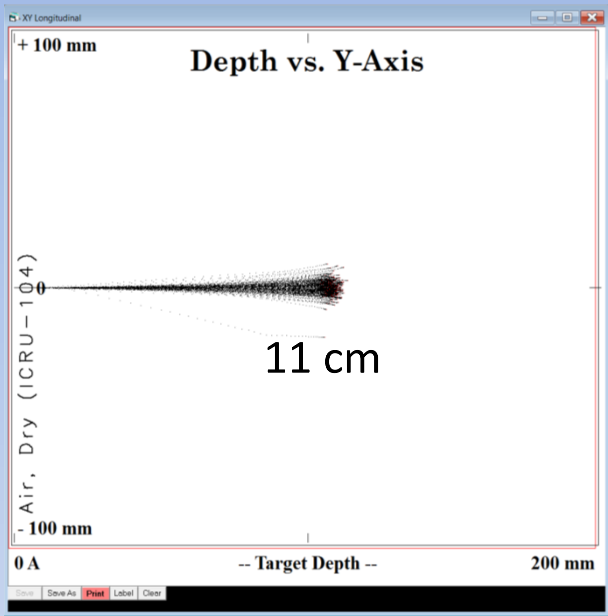


Analysis of H, Li, B, C, N, O

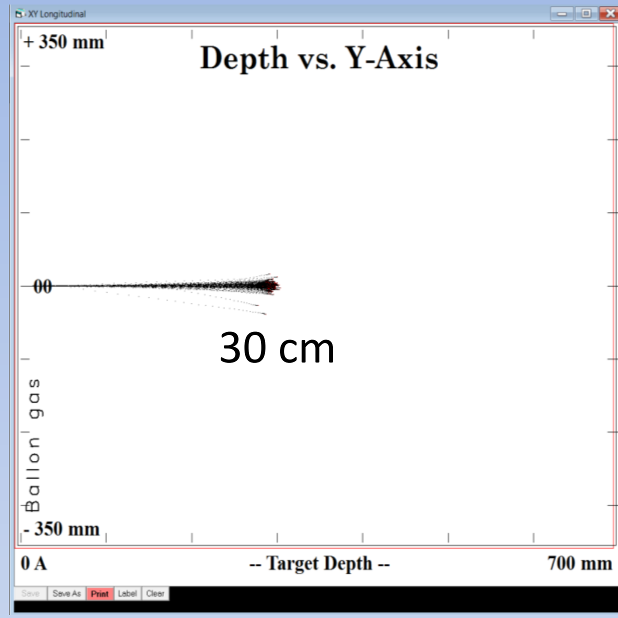
- difficult to detect with conventional RBS
- not detectable with PIXE
- High energy ERDA or NRA not applicable to ambient conditions

Approach: combined RBS and coincidence ERDA using a MeV proton beam

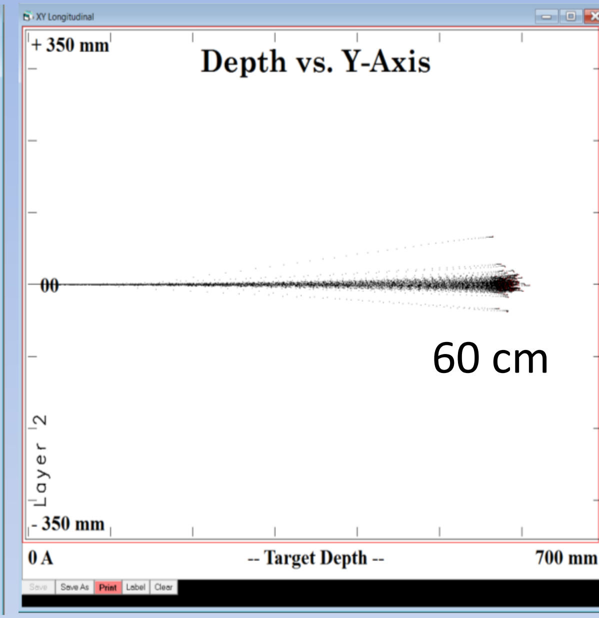
Range of 2.5MeV protons in air

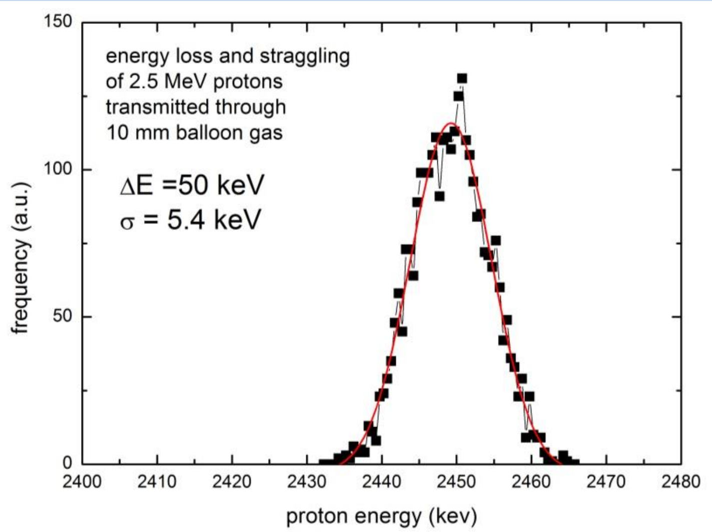


Range of 2.5MeV protons in balloon gas



Range of 2.5MeV protons in Helium gas



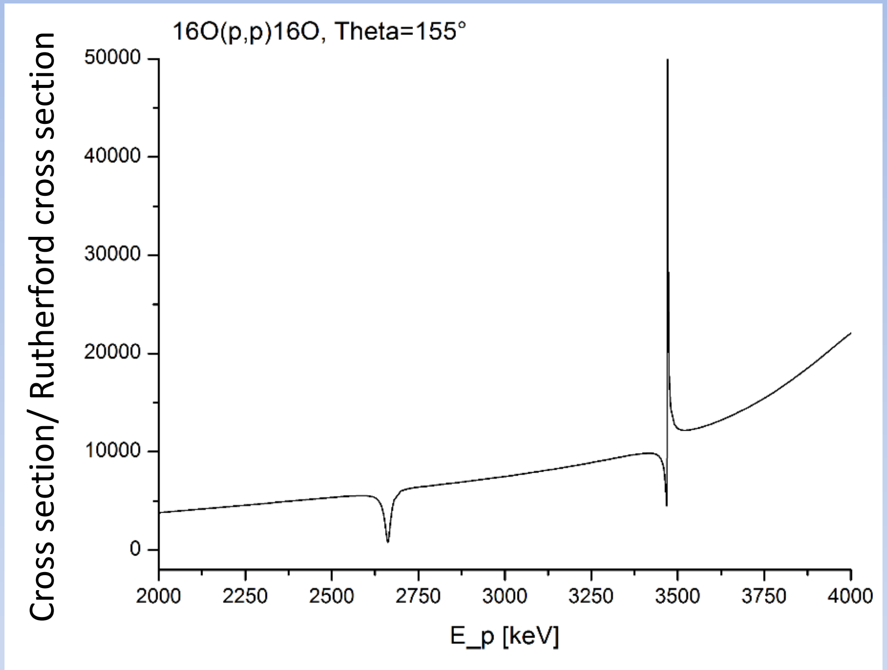


Use balloon gas as ambient condition:

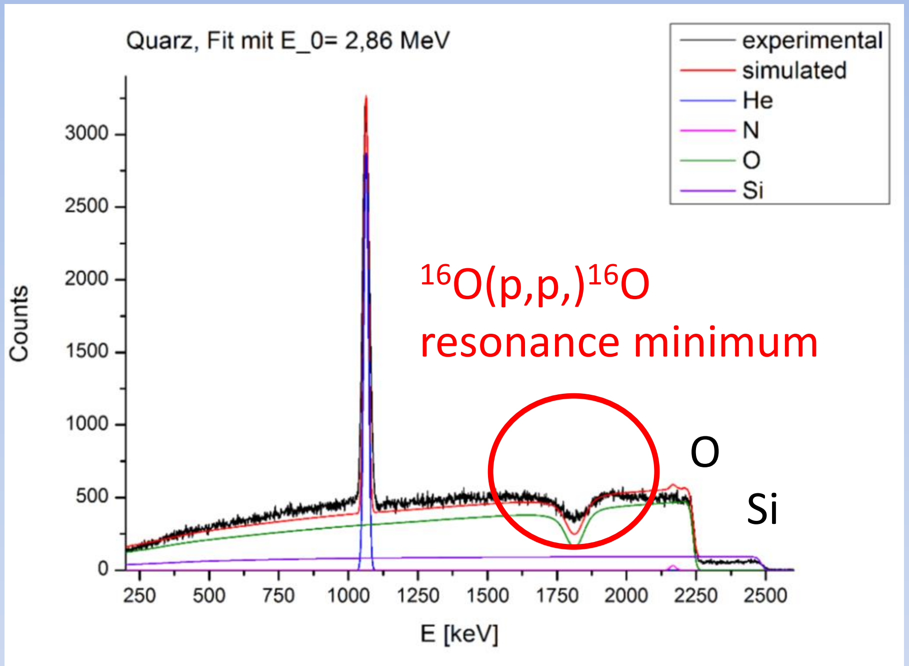
- ✓ large ion range of 30 cm
- ✓ little angular straggling
- ✓ acceptable energy straggling σ = 5.4 keV
- ✓ low cost of ballon gas
- – 50 keV energy loss in 10 mm balloon gas

High non-Rutherford scattering cross section for light elements

Non Rutherford cross section for $^{16}O(p,p)^{16}O$



RBS spectrum of SiO_2 with E=2.86 MEV



Restrict the energy of incident protons to 2.6 MeV

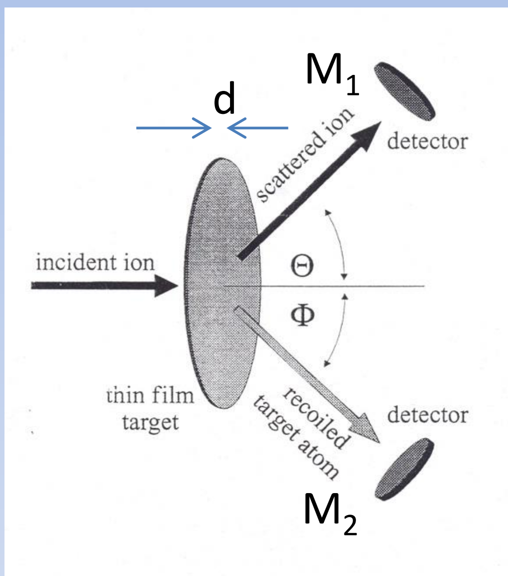
Conditions for external proton beam IBA

ballon gas ; $E_p \leq 2.6$ MeV ; traversed gas volume: 10 mm

Hydrogen Coincidence ERDA with external proton beam

Elastic Recoil Detection Analysis

H. Hofsäss, J. Tirira, Y. Serruys and P. Trocellier, in **Forward Recoil Spectrometry**: Applications to Hydrogen Determination in Solids, Chapter 9, J. Tirira, Y. Serruys and P. Trocellier (eds.), (Plenum Press, New York, 1996, ISBN 0-306-45249-9) p.209-246



$$\tan\theta = \frac{\sin 2\phi}{\frac{M_1}{M_2} - \cos(2\phi)}$$

Special case $M_1 = M_2$: kinematic factors K, Λ and ΔE(x)

$$K = \cos^2\theta$$

$$\Lambda = \cos^2\phi$$

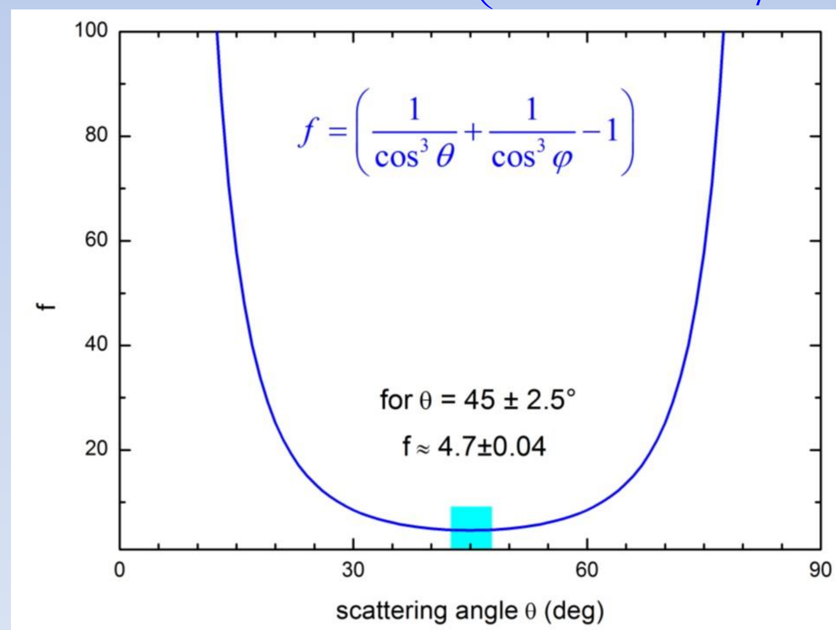
$$K + \Lambda = 1$$

$$\tan\theta = \cot\phi$$

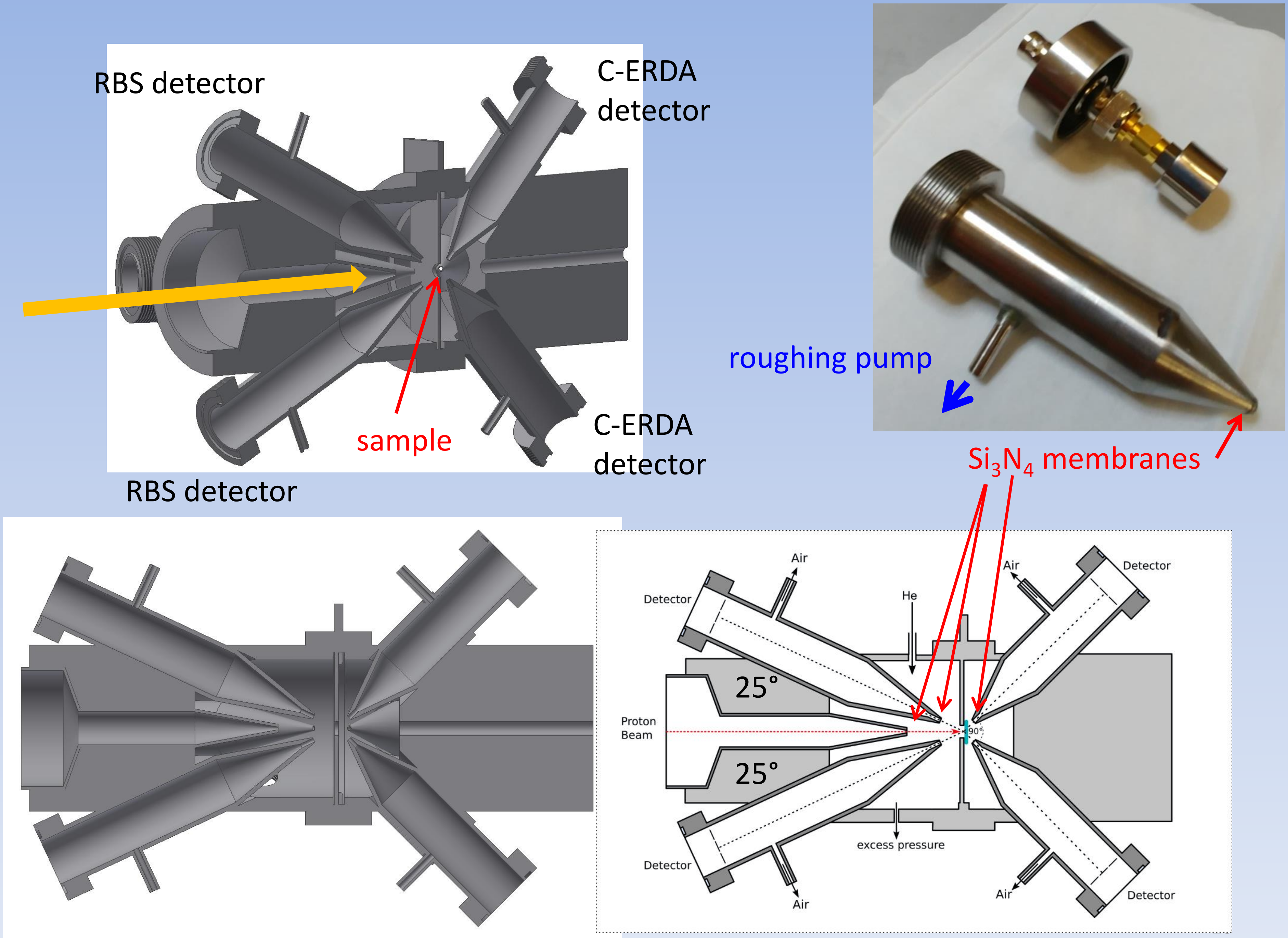
$$\cos^2\theta + \cos^2\phi = 1$$

$$\theta + \phi = \pi / 2$$

$$\Delta E(d) = S_{E_0}\cdot d + S_{E_0}\cdot x\left(\frac{1}{\cos^3\theta} + \frac{1}{\cos^3\varphi} - 1\right)$$

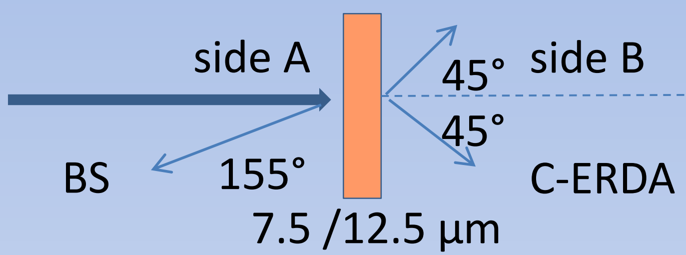


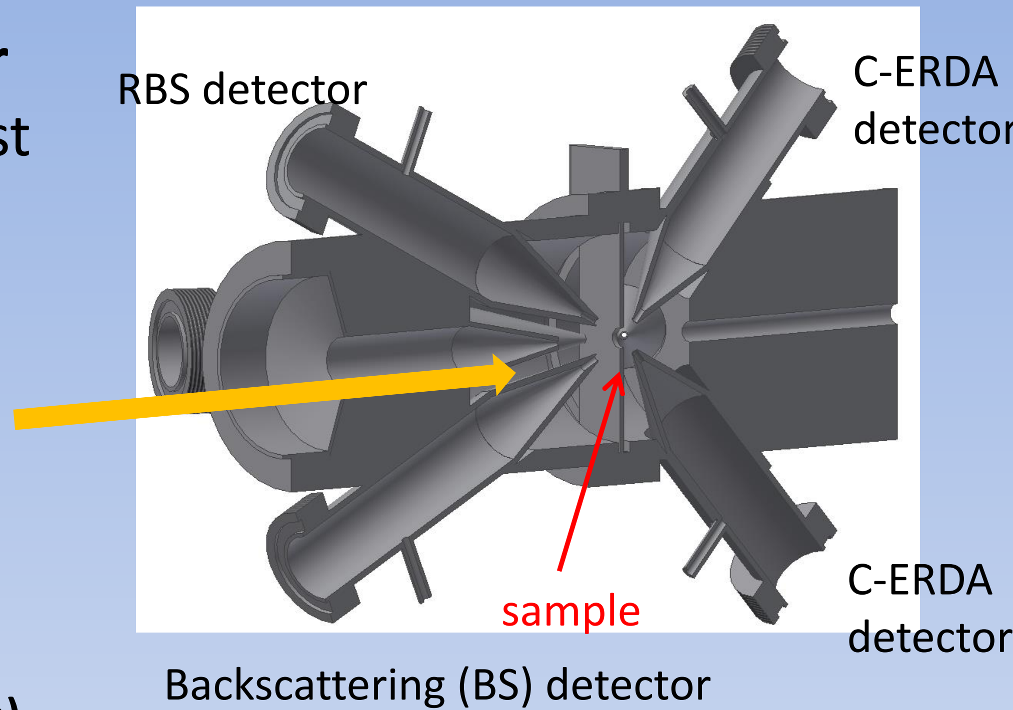
Detection at θ = ϕ = 45°±2.5° allows depth resolved analysis of Hydrogen profiles


RBS detector
C-ERDA detector
sample
C-ERDA detector
RBS detector
roughing pump
Si_3N_4 membranes
Air
Detector
He
Air
Detector
25°
Proton Beam
90°
25°
excess pressure
Detector
Air
Air
Detector

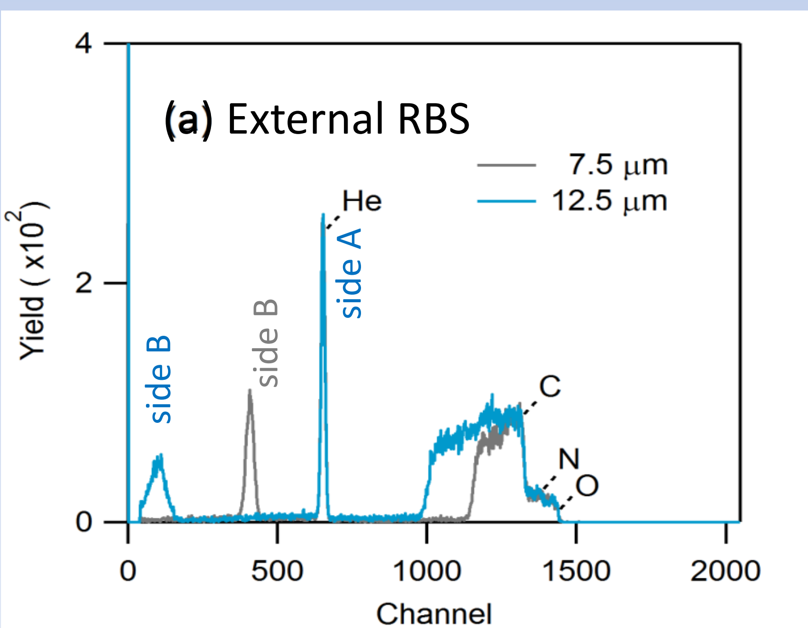
External proton beam setup for

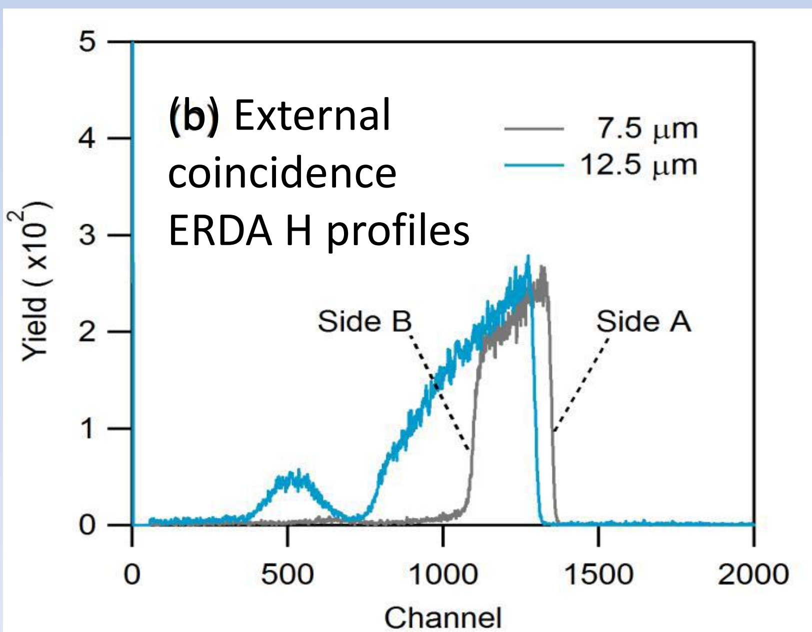
- light element analysis in moist samples and thin films





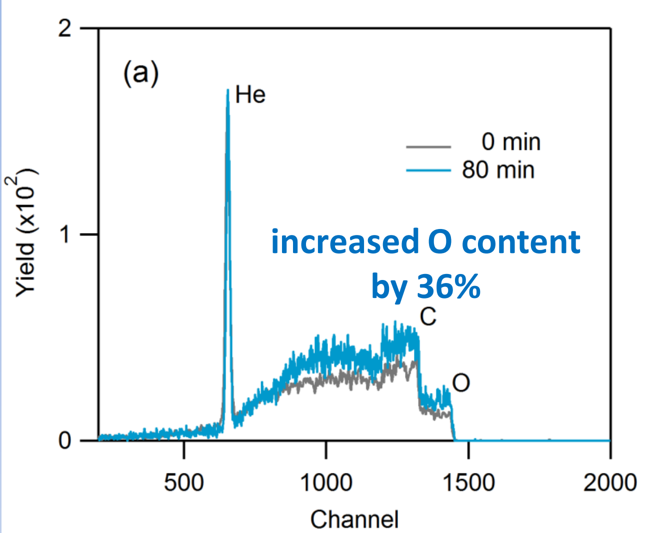
Analysis of polyimide films (Kapton)

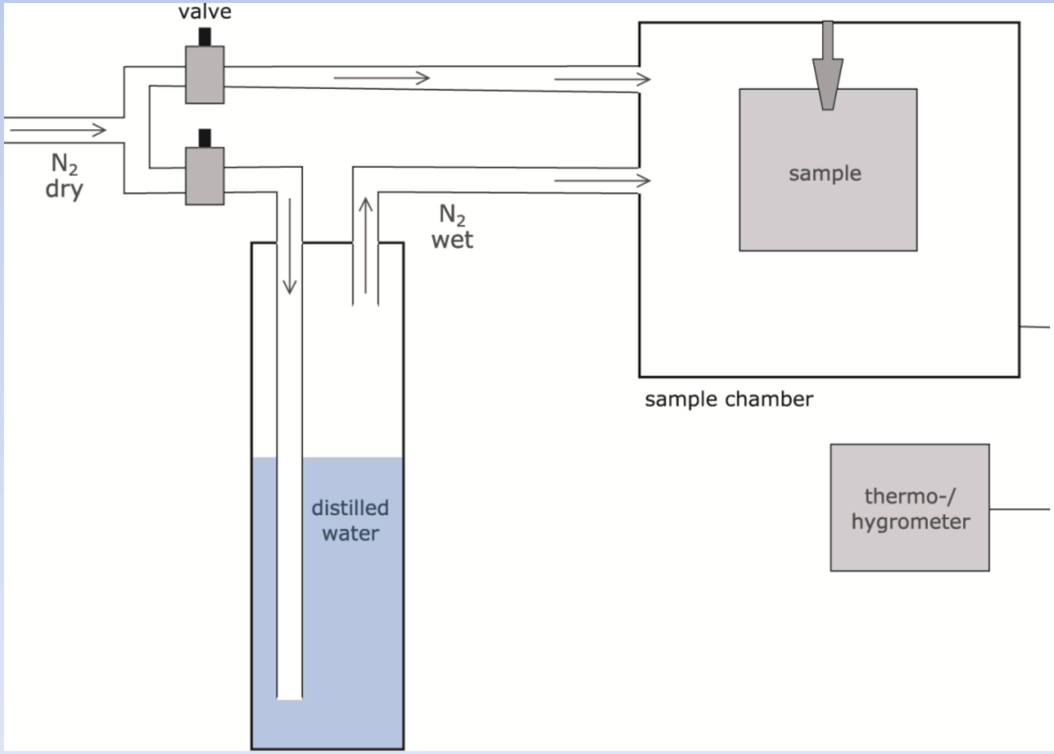




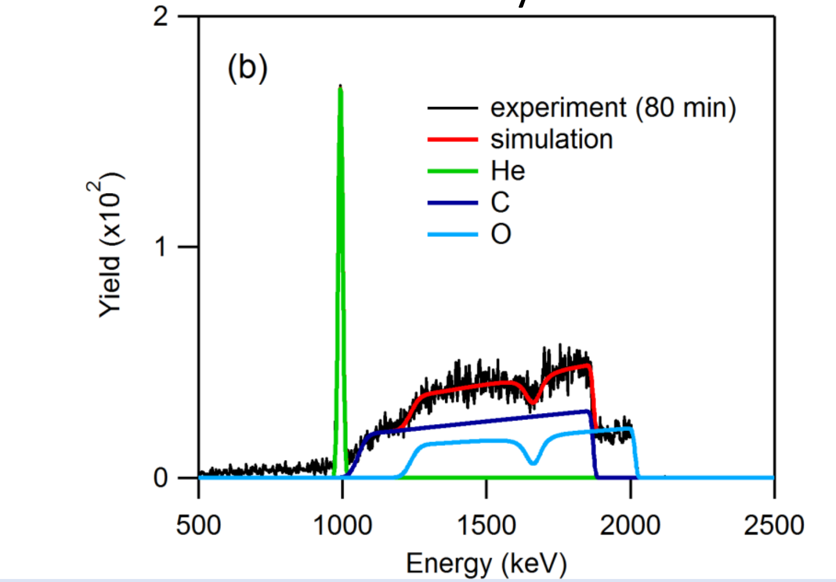
Example: Hydrogen analysis of moist samples

- 25 µm poly(vinyl alcohol) (PVA) thin flim samples
- Stored in vacuum for 48 h
- Exposed to wet N_2- gas for t= 0 – 80 min
- Ext. Beam RBS ➔ higher O content for t=80 min
- Ext. Beam C-ERDA



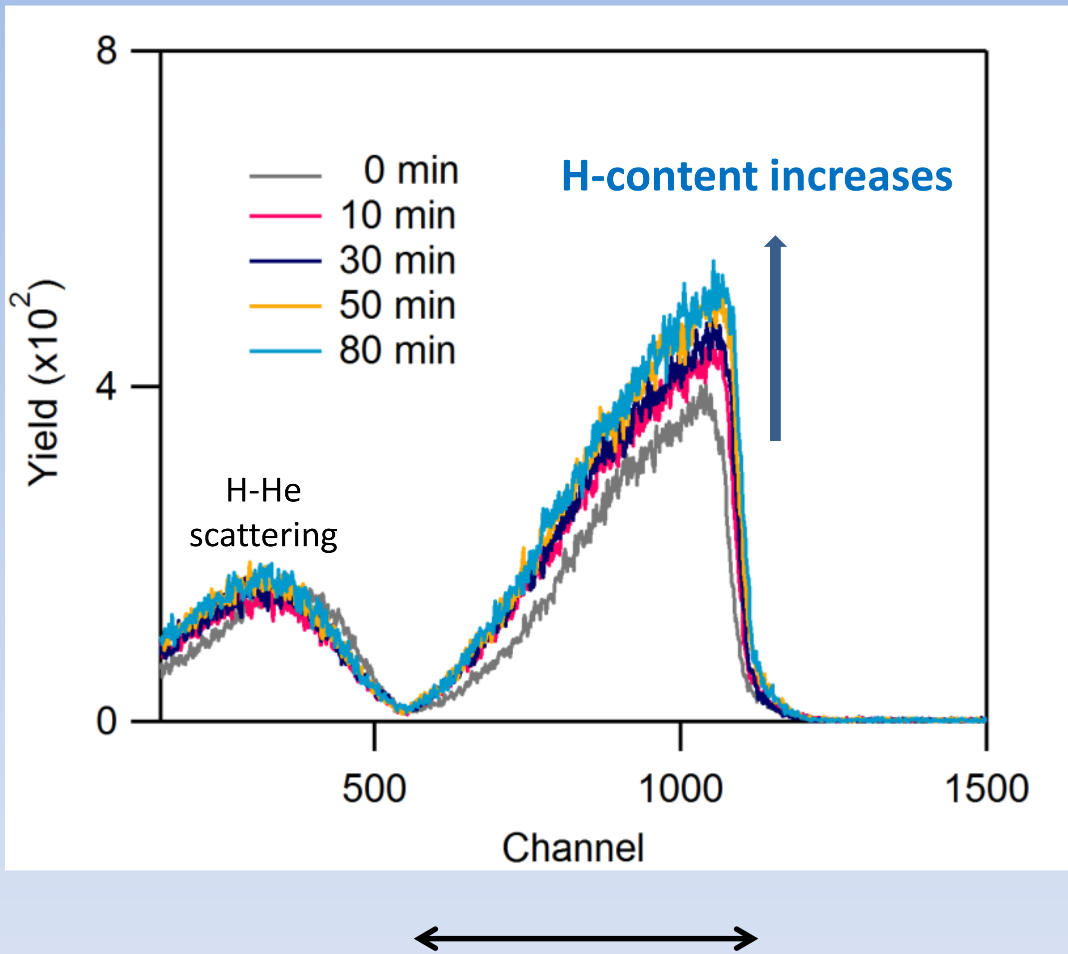


SIMNRA analysis

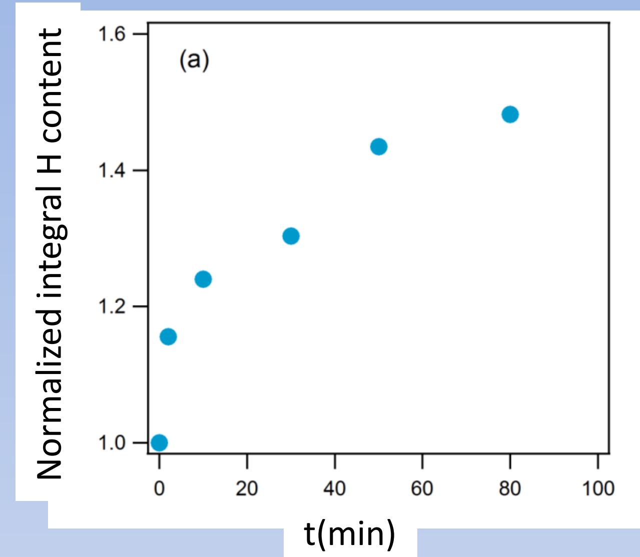


Example 3: Hydrogen analysis of moist samples

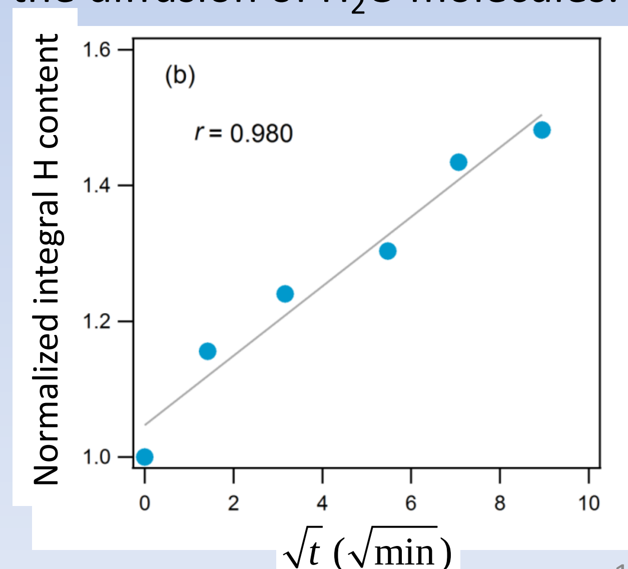
C-ERDA Hydrogen profile of moist PVA



≈ 10 µm

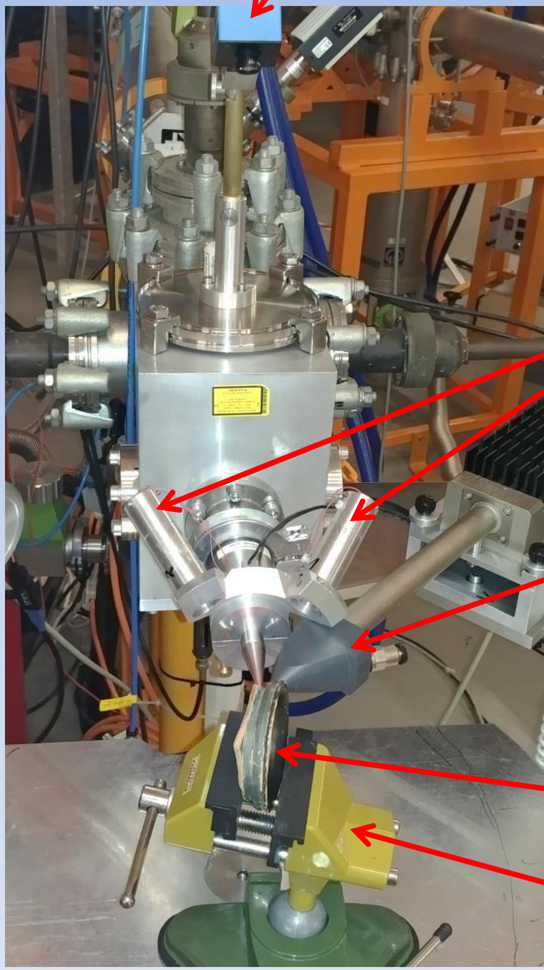


water absorption is dominated by the diffusion of H_2O molecules.

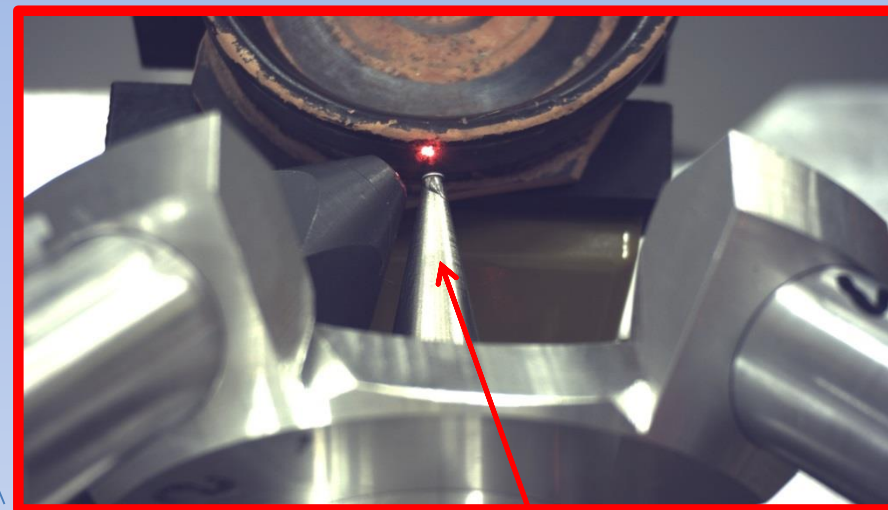


External beam setup for PIXE
Particle induced X-ray emission)

sample camera



adjustement
lasers



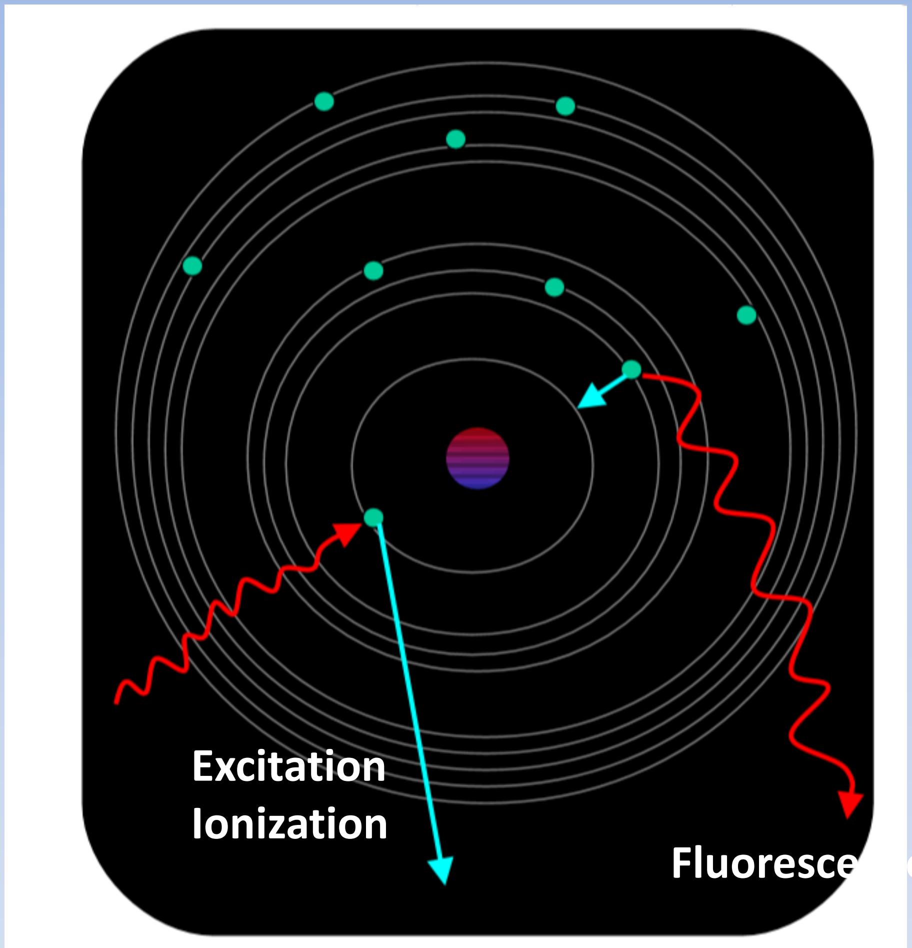
Beam extraction nozzle

KETEK X-ray SDD detector

sample

Lab vise with
multidirectional vise head

Basics of X-ray spectrometry for element analysis

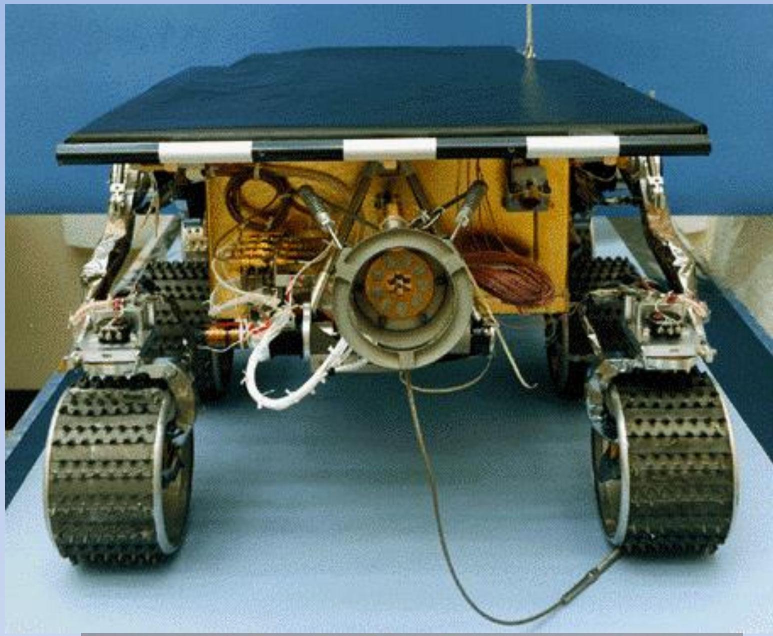


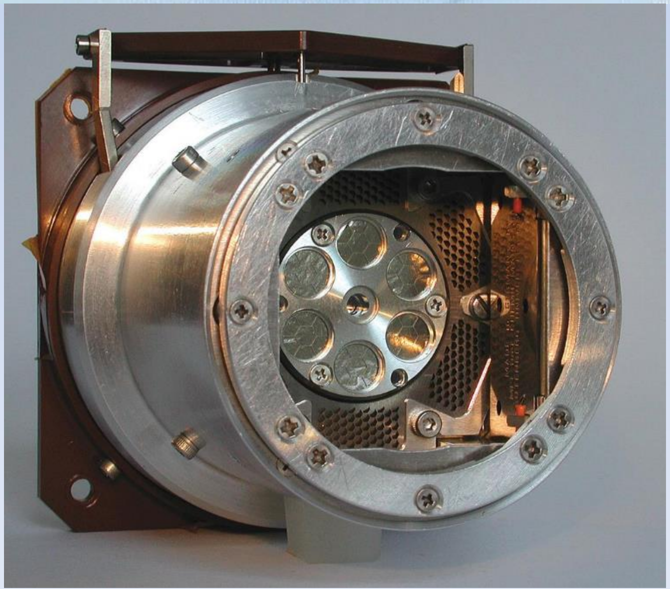
Excitation:

- **Electrons**
  - **EDX energy dispersive X**
- **X-rays**
  - **XRF X-ray fluorescence**
  - **ED XRF (energy dispersive)**
  - **WD XRF (wave length dispersive)**
  - **TXRF (total reflection)**
- **Gamma radiation**
  - **Similar to XRF**
- **Protons**
  - **PIXE**
- **Alpha particles**
  - **PIXE: the Mars version**

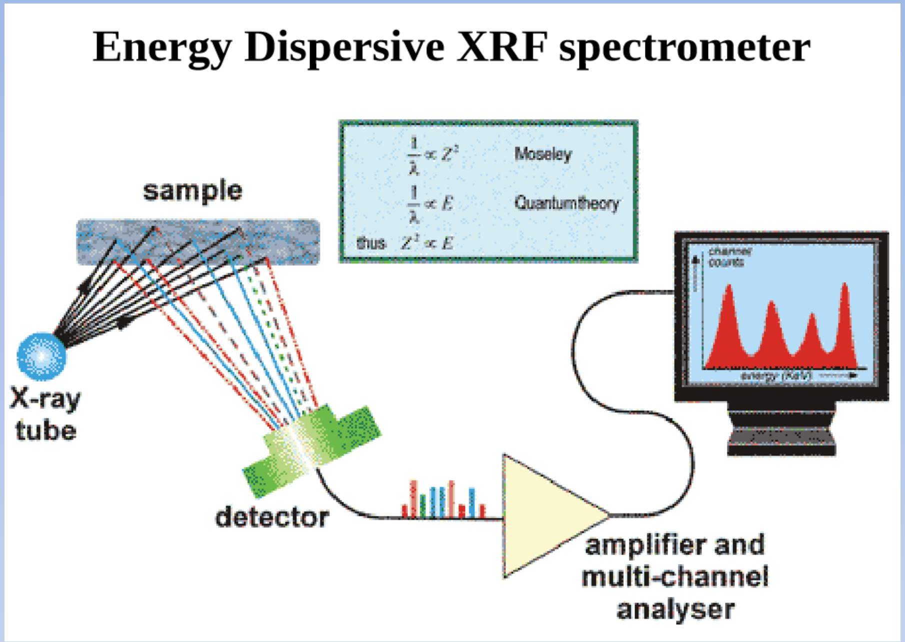
Alternatives: Neutron activation analysis
Inductively coupled plasma mass spectrometry (ICP-MS)

Particle Induced X Ray Emission and Mars Exploration Rovers

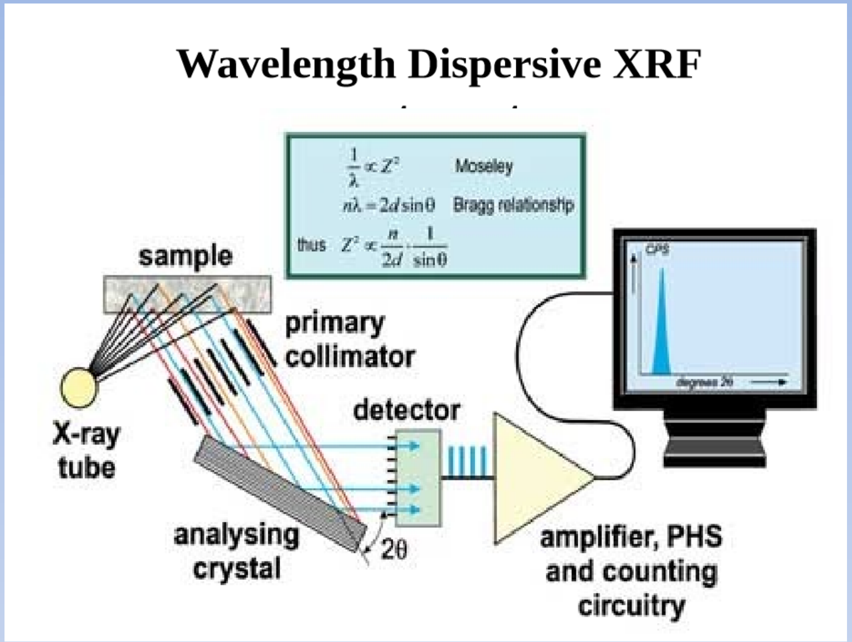




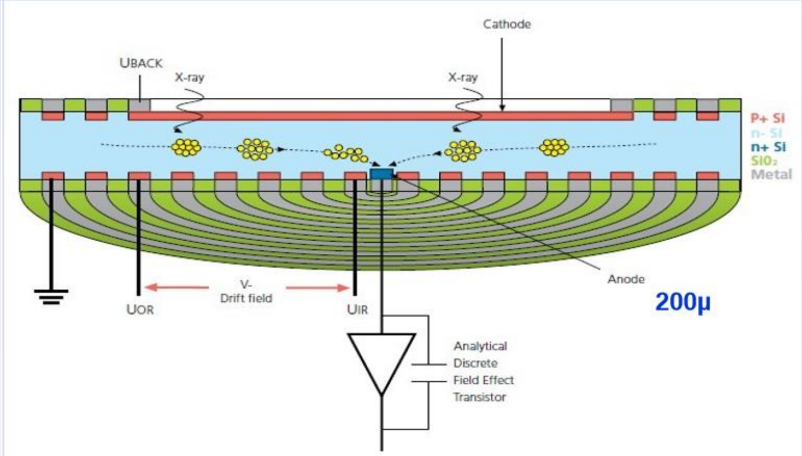
Alpha Source: Curium ^{244}Cm produces alphas and X-rays from ^{240}Pu decaqy fast, energy resolution 150 eV



slow, very high energy resolution of few eV



Si drift detectors

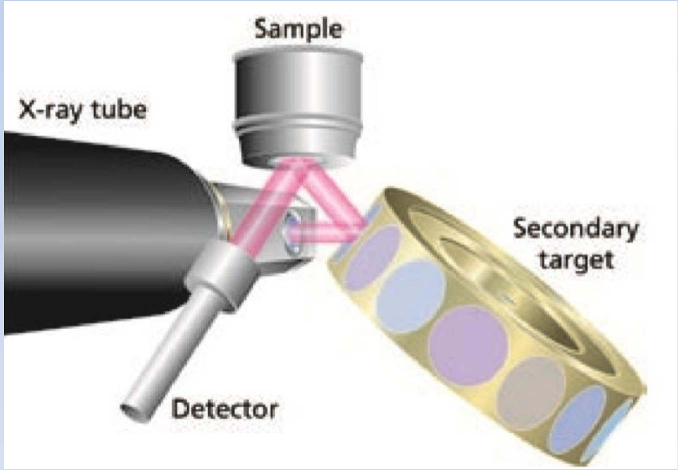


Braggs law: $n\lambda = 2d\sin\theta$

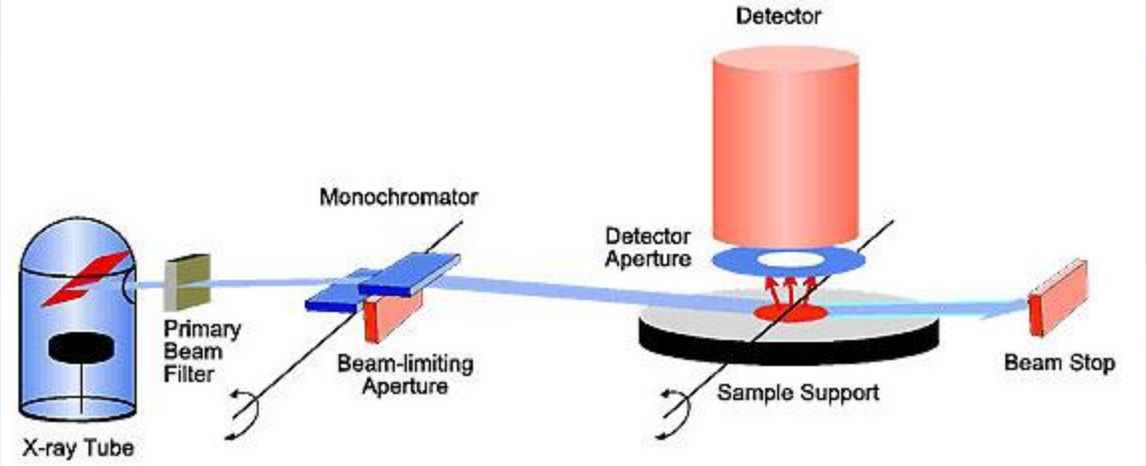
XRF:

- **The commercial technique**
- **Hand held** plug-and-play systems (X-ray flash light)
- Background from backscattered X-rays
- Background from Compton Photons
- Bremsstrahlung from Compton electrons
- Divergent X-ray beam

3d X-ray optics for low background analyses



Total reflection XRF for low background high sensitivity analyses



So why protons to excite atoms ?

S. Johansson et al., BULLETIN OF THE AMERICAN PHYSICAL SOCIETY 23 (1978) 1035
University Lund, Sweden
Johansson, S. A. E. and Campbell. J. L. 'PIXE: A Novel Technique for Elemental Analysis', Wiley, Chichester, 1988.

- **Well defined ion range** ↔ all X-rays are generated in the same sample volume

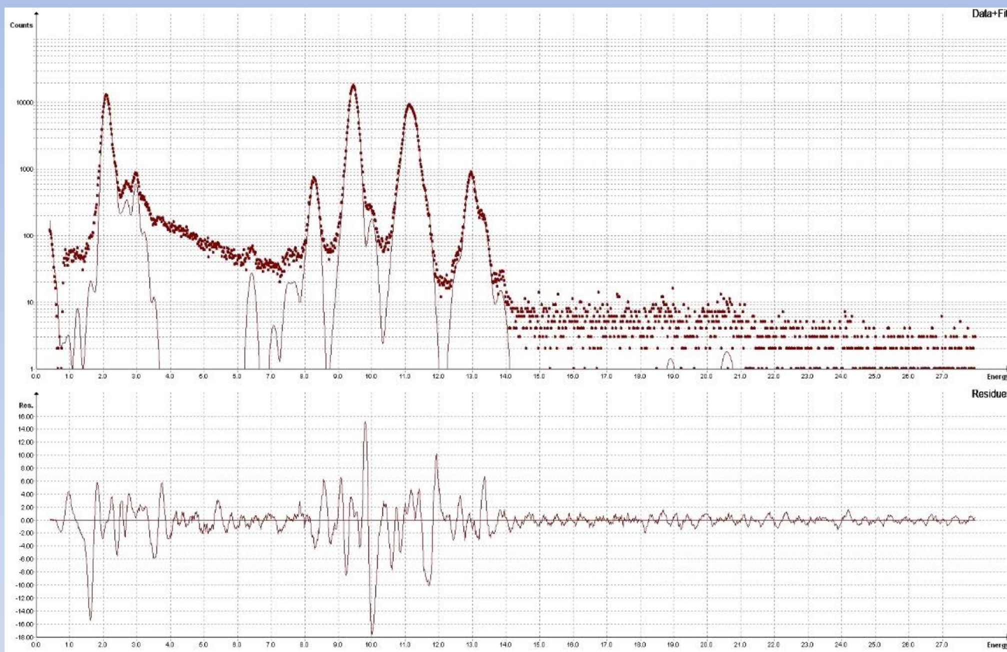
  40 keV X-rays: 200 – 2000 µm half thickness
  2500 MeV protons: 30 µm in typical metal alloys
  100 µm in polymers, paint etc

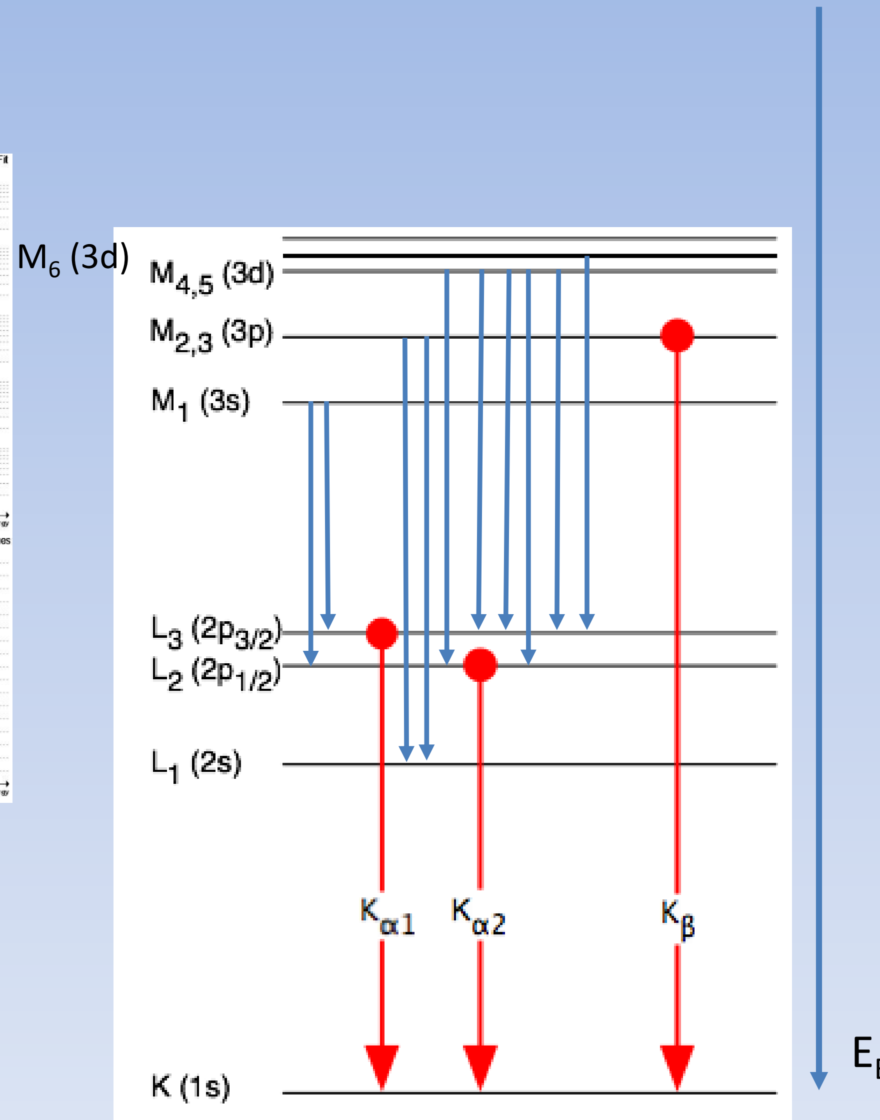
- **Excitation/ionization better for light elements**
  - Photo effect $\sigma \sim \frac{Z^5}{E^{.5}}$
- **Almost now Bremsstrahlung background** $I_{brems} \sim \frac{1}{m^2}$
  - Compared to electrons background is reduced by factor **$3 \cdot 10^6$**
- **No backscattered photons**
- **Combination with Backscattering spectrometry and gamma exitation spectrometry (PIGE)**

- **Quantitative**
  - ion energy loss
  - ionization cross section
- **Invisible elements** like Oxygen included in the analysis

Analysis with GUPIXWIN from University Guelph, Canada

PIXE spectrum of a Platinum foil

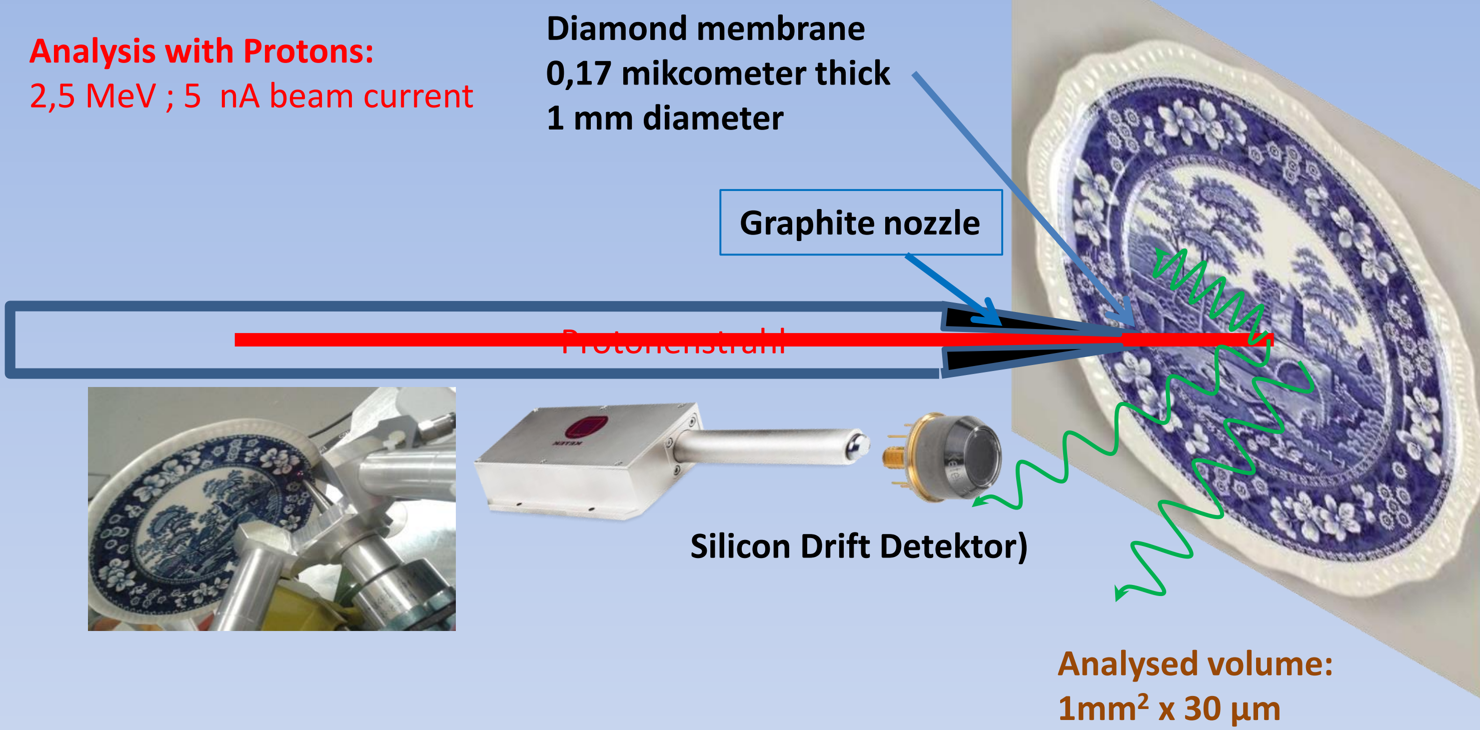




But also transitions from N,O,P Orbitals to L- and M -shell

Up to 12 K-shell X-ray lines
Up to 25 L – and M X-ray lines per Element

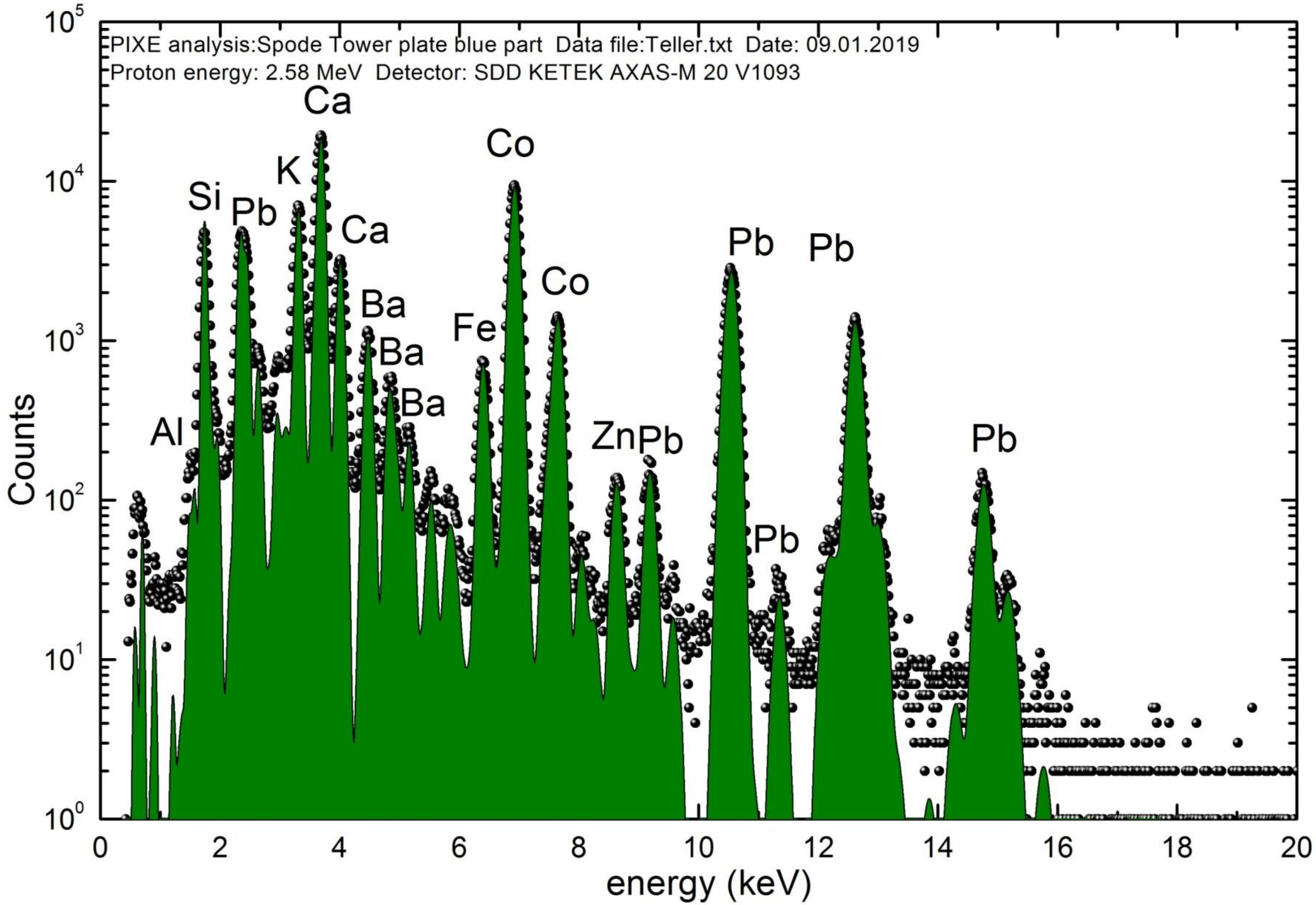
Lab course example: analysis of a british desert plate

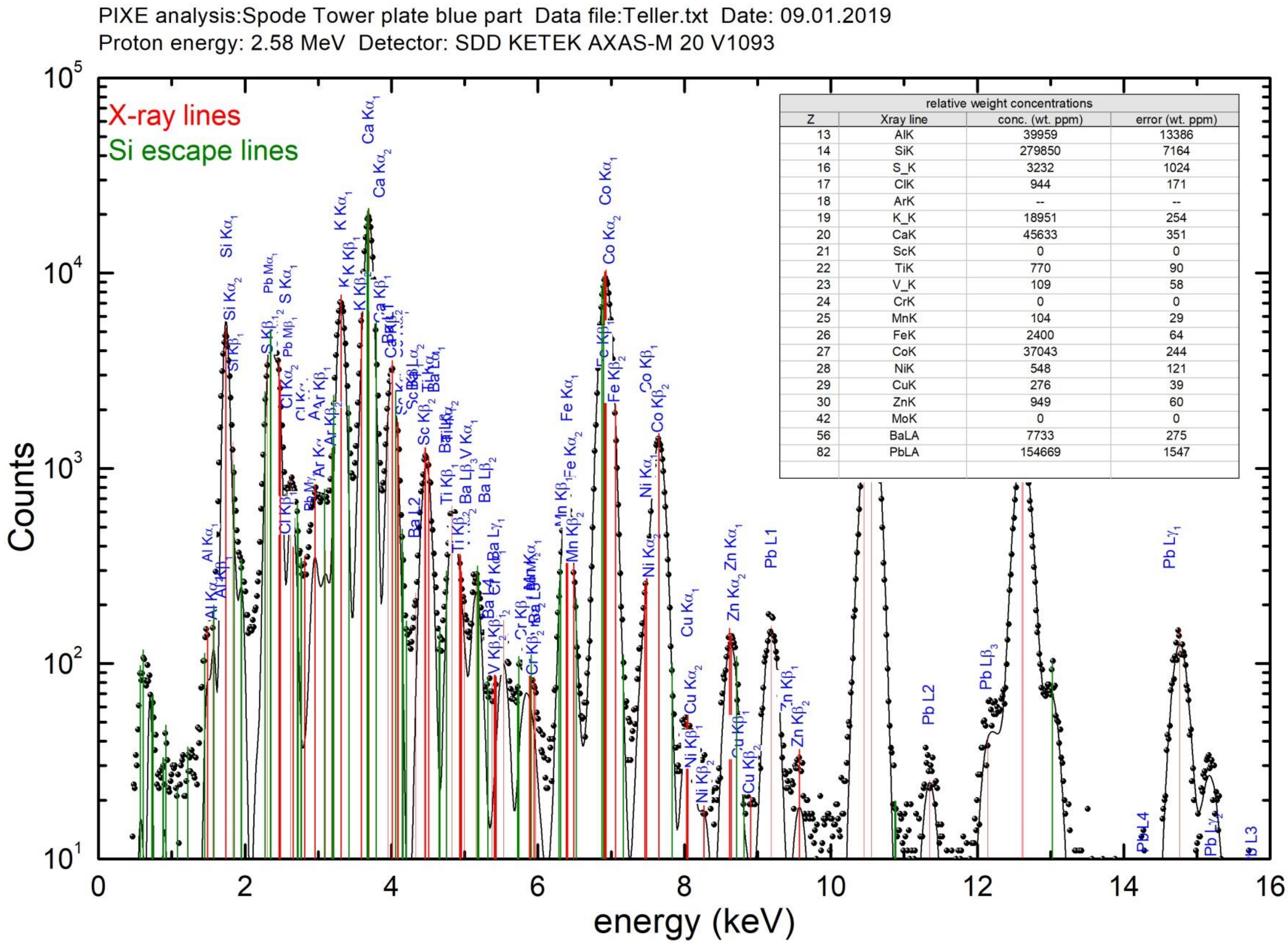


- Spode Copeland –Blue Tower Series since 1814
- Until 1860: Ultramarine blue made from **Lapislazuli** $Na_6[Al_6Si_6O_{24}]S_xCa$

- Until 1894: Royal saxon blue made from **Azurite** $Cu_3(CO_3)_2(OH)_2$

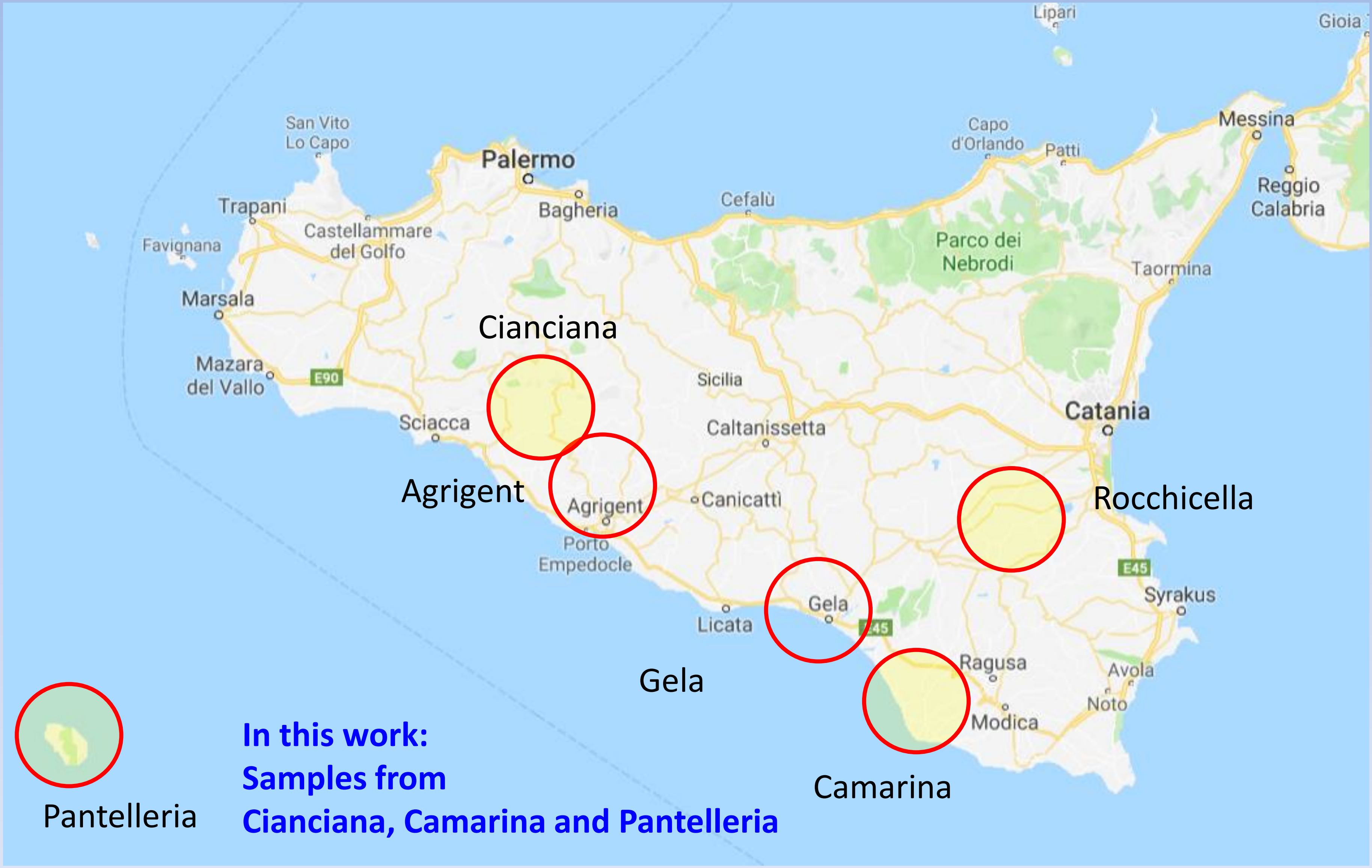
- Since 1986: Zaffres Blue made of Cobalt oxide


PIXE analysis:Spode Tower plate blue part Data file:Teller.txt Date: 09.01.2019
Proton energy: 2.58 MeV Detector: SDD KETEK AXAS-M 20 V1093
Al
Si
Pb
K
Ca
Ca
Ba
Ba
Ba
Fe
Co
Co
Zn
Pb
Pb
Pb
Pb
Pb
Counts
energy (keV)
10^5
10^4
10^3
10^2
10^1
10^0
0
2
4
6
8
10
12
14
16
18
20



Z	Xray line	conc. (wt. ppm)	error (wt. ppm)
13	AlK	39959	13386
14	SiK	279850	7164
16	S_K	3232	1024
17	ClK	944	171
18	ArK	--	--
19	K_K	18951	254
20	CaK	45633	351
21	ScK	0	0
22	TiK	770	90
23	V_K	109	58
24	CrK	0	0
25	MnK	104	29
26	FeK	2400	64
27	CoK	37043	244
28	NiK	548	121
29	CuK	276	39
30	ZnK	949	60
42	MoK	0	0
56	BaLA	7733	275
82	PbLA	154669	1547

Archeological Survey in Sicily



In this work:
Samples from
Cianciana, Camarina and Pantelleria

Ceramic samples were collected at the ground, no excavation

GEORG-AUGUST-UNIVERSITÄT GÖTTINGEN
ARCHÄOLOGISCHES INSTITUT

Fritz Thyssen Stiftung für Wissenschaftsförderung

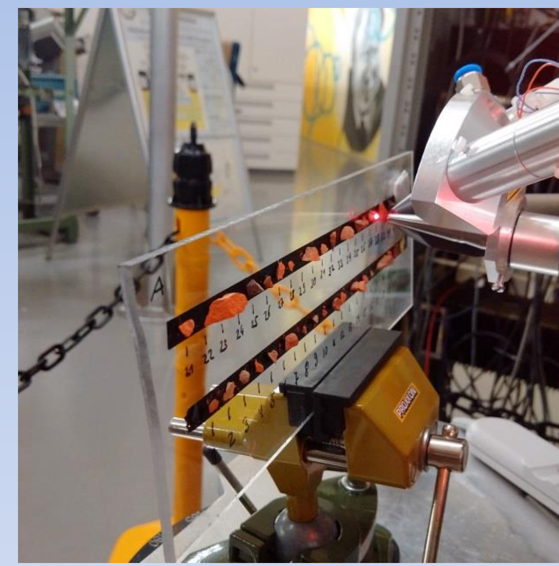
GERDA HENKEL STIFTUNG

DFG

- Pottery samples are documented using GPS and Photography and registered in topograhical maps including the context
- Samples remain in archives in Italy
- Tiny fragments of few mm^3 , which usually are being thrown away, were brought to Göttingen with local permission.

External beam setup for PIXE

- Samples were mounted on adhesive carbon tape or plasticine
- Each sample was aligned with surface perpendicular to the beam using:
  - Two-Laser-pointer beam spot alignment
  - Lab vise with multidirectional vise head



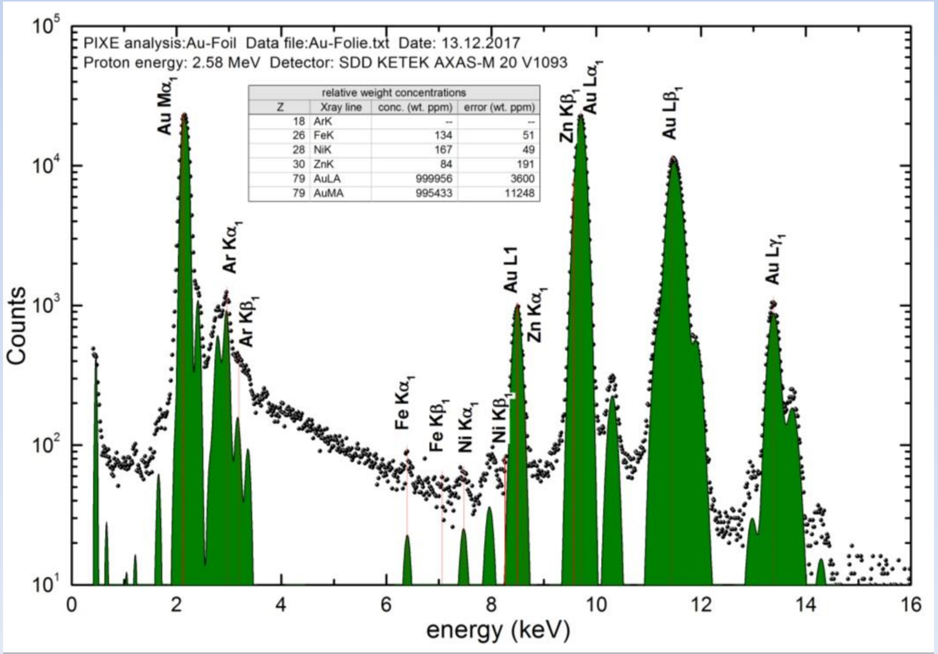
Total: 550 samples analyzed

Analysis: Beam energy 2660 keV ; beam current ≈ 3-5 nA ; acquisition time: 120 s
Window: 200 nm Si_3N_4 1x1 mm^2 membrane or
170 nm 1mm diameter diamond membrane
Energy at the sample surface 2580 ± 7 keV
KETEK SDD 450 µm, 8µm Be window, 5mm diameter, 43 mm air absorber

Calibration samples:

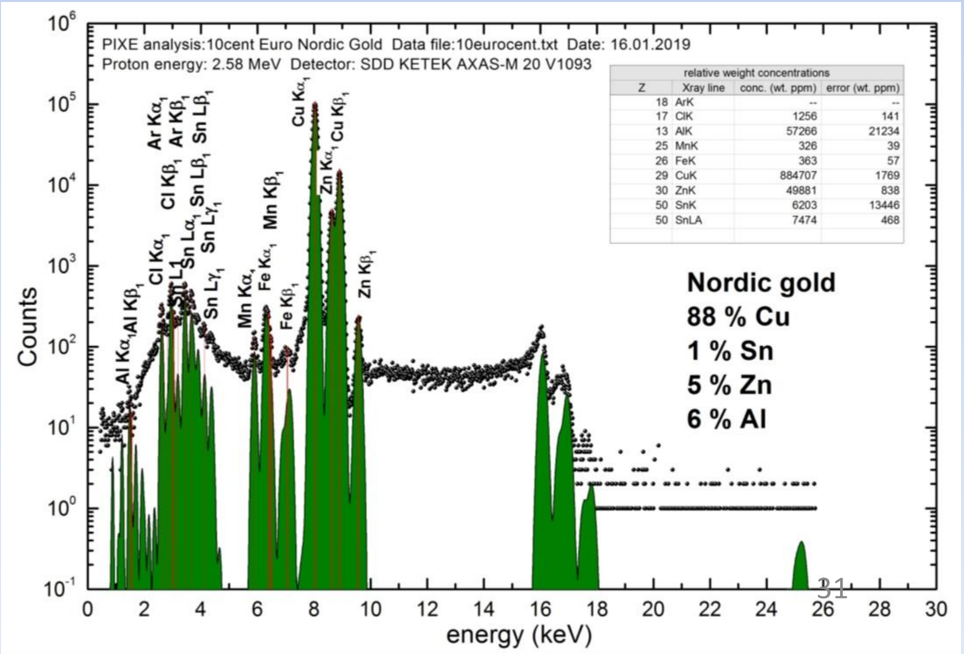
- **Au foil** Au-M lines at 2 keV, Au L lines at 9-14 keV
  - Verifies the detector efficiency between 2 keV and 14 keV
- **Eurocent coin** made of „Nordic gold“
  - Reproduce the nominal content of 88% Cu, 1% Sn, 5% Zn, 6% Al
  - Verifies the detector efficiency in the energy regime 1.5 keV – 10 keV

PIXE spectrum of a Au foil



relative weight concentrations			
Z	Xray line	conc. (wt. ppm)	error (wt. ppm)
18	ArK	--	--
26	FeK	134	51
28	NiK	167	49
30	ZnK	84	191
79	AuLA	999956	3600
79	AuMA	995433	11248

PIXE spectrum of a 10 Eurocent coin

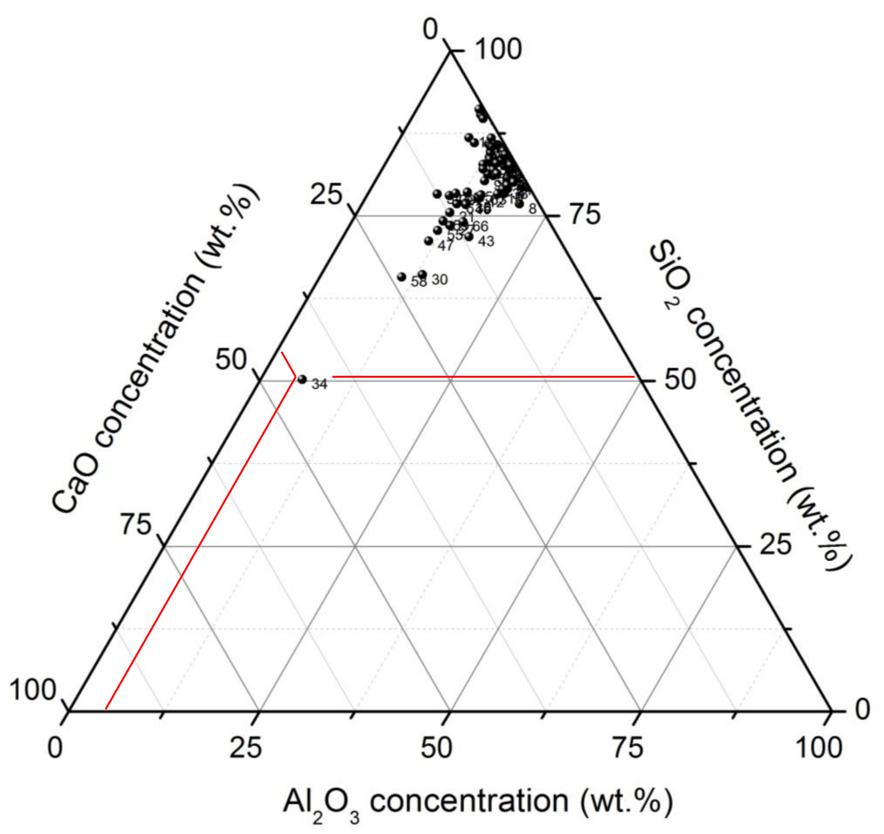


relative weight concentrations			
Z	Xray line	conc. (wt. ppm)	error (wt. ppm)
18	ArK	--	--
17	ClK	1256	141
13	AlK	57266	21234
25	MnK	326	39
26	FeK	363	57
29	CuK	884707	1769
30	ZnK	49881	838
50	SnK	6203	13446
50	SnLA	7474	468

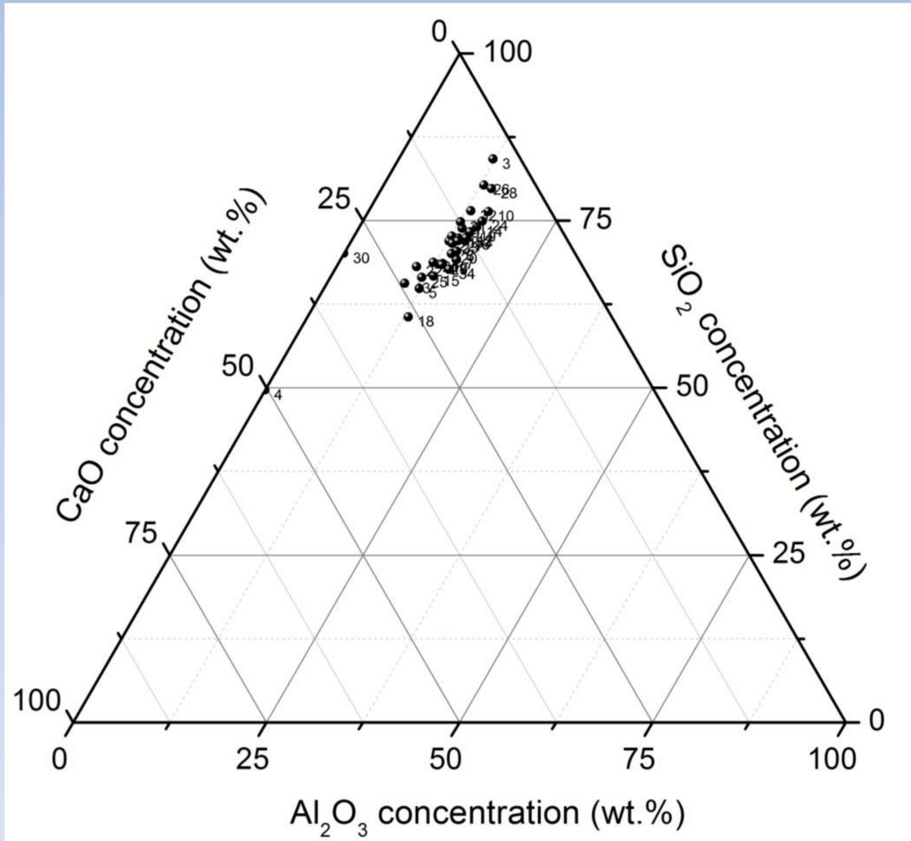
Results

Balance between SiO_2 –CaO and Al_2O_3

Terra Sigillata
(Roman ceramic table ware)

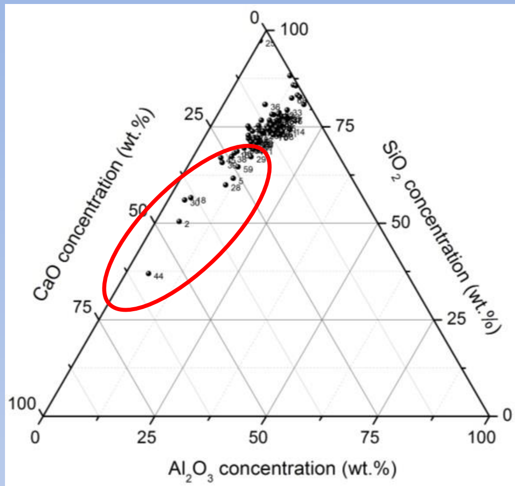


Pre-historical pottery

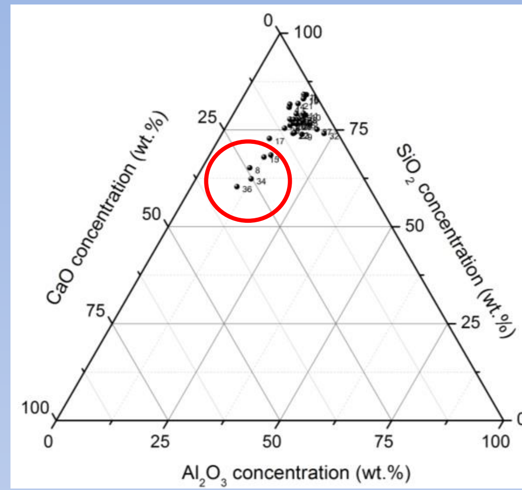


(Note: concentrations are normalized to 100 %)

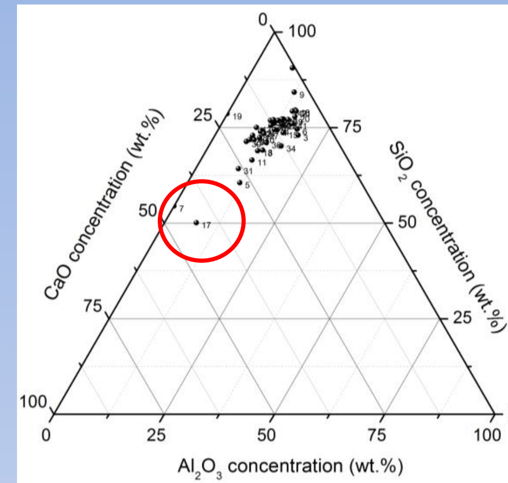
Camarina 27-08-18



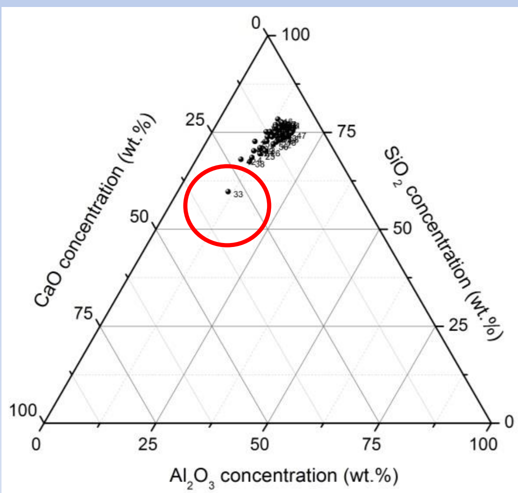
Camarina 15-12-17



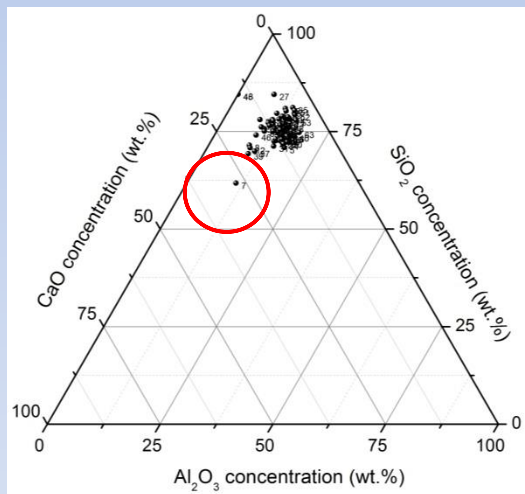
Camarina 26-07-18



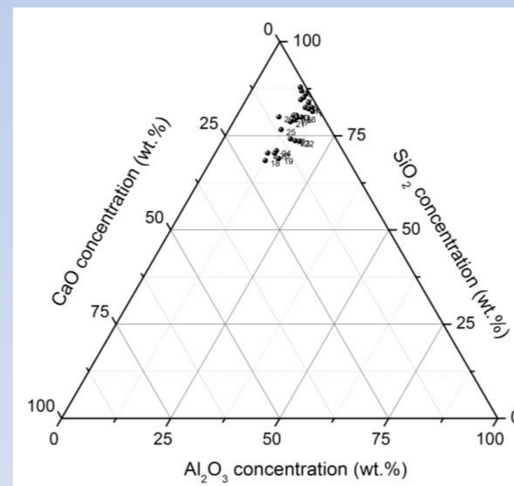
Camarina 19-12-17



Camarina 28-02-18

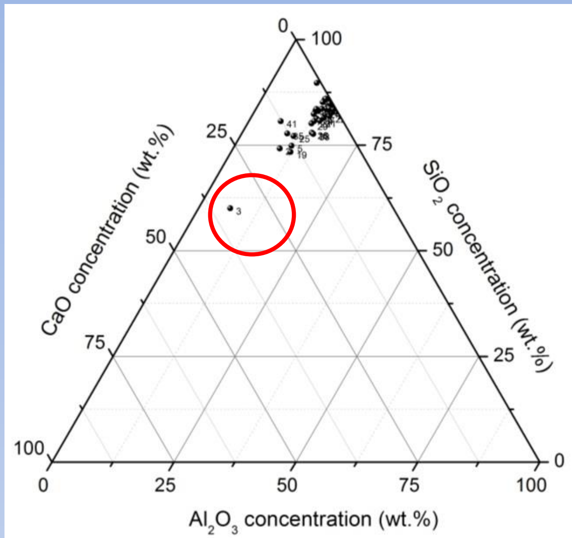


Camarina 30-08-18

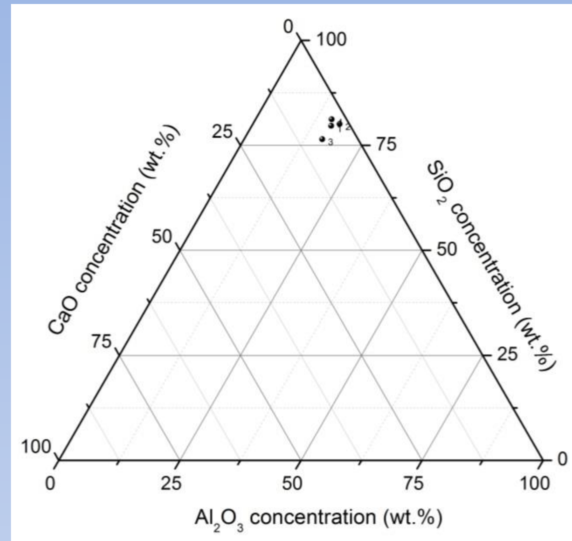


- Typical: SiO_2 75 wt.% , CaO: 13 wt.% , Al_2O_3 14 wt.% (relative)
- **Some samples with very high content of CaO of 25-50 wt.%**
- Few samples with very little CaO (Terra Sigillata, African cooking ware)

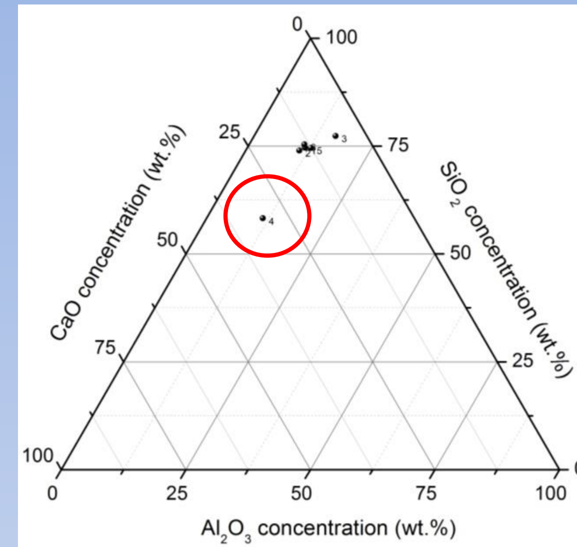
African cooking ware



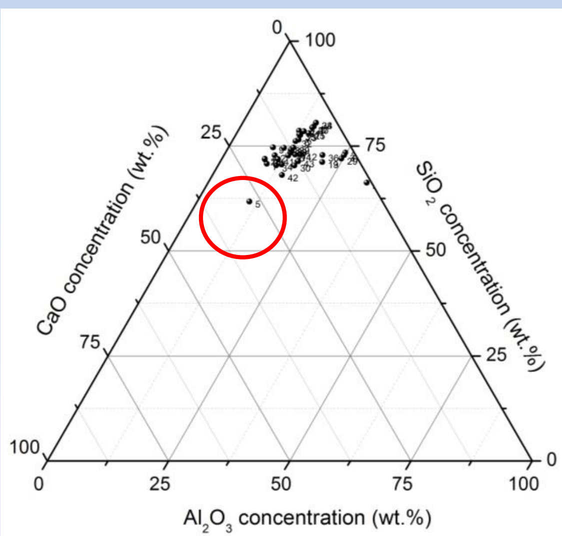
Rocchicella



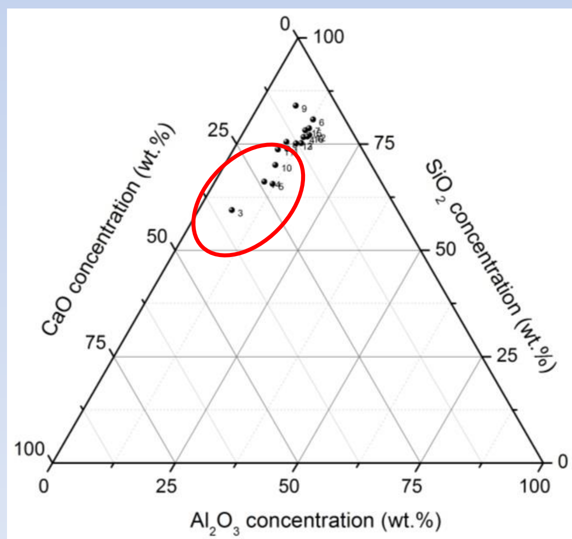
Domestic pottery



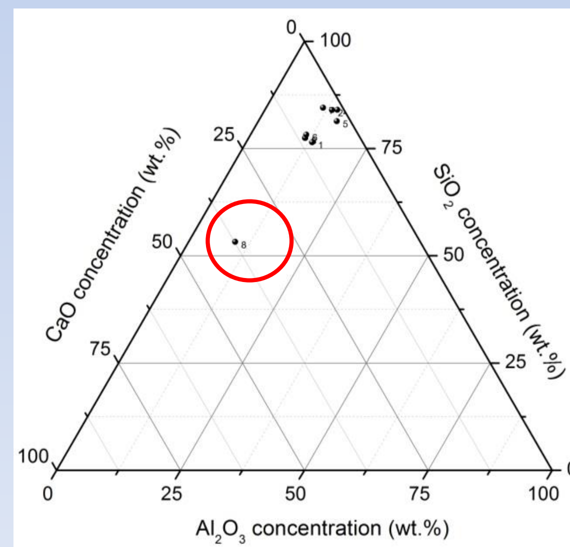
Greek laquer ware
(Greek fine ceramics)



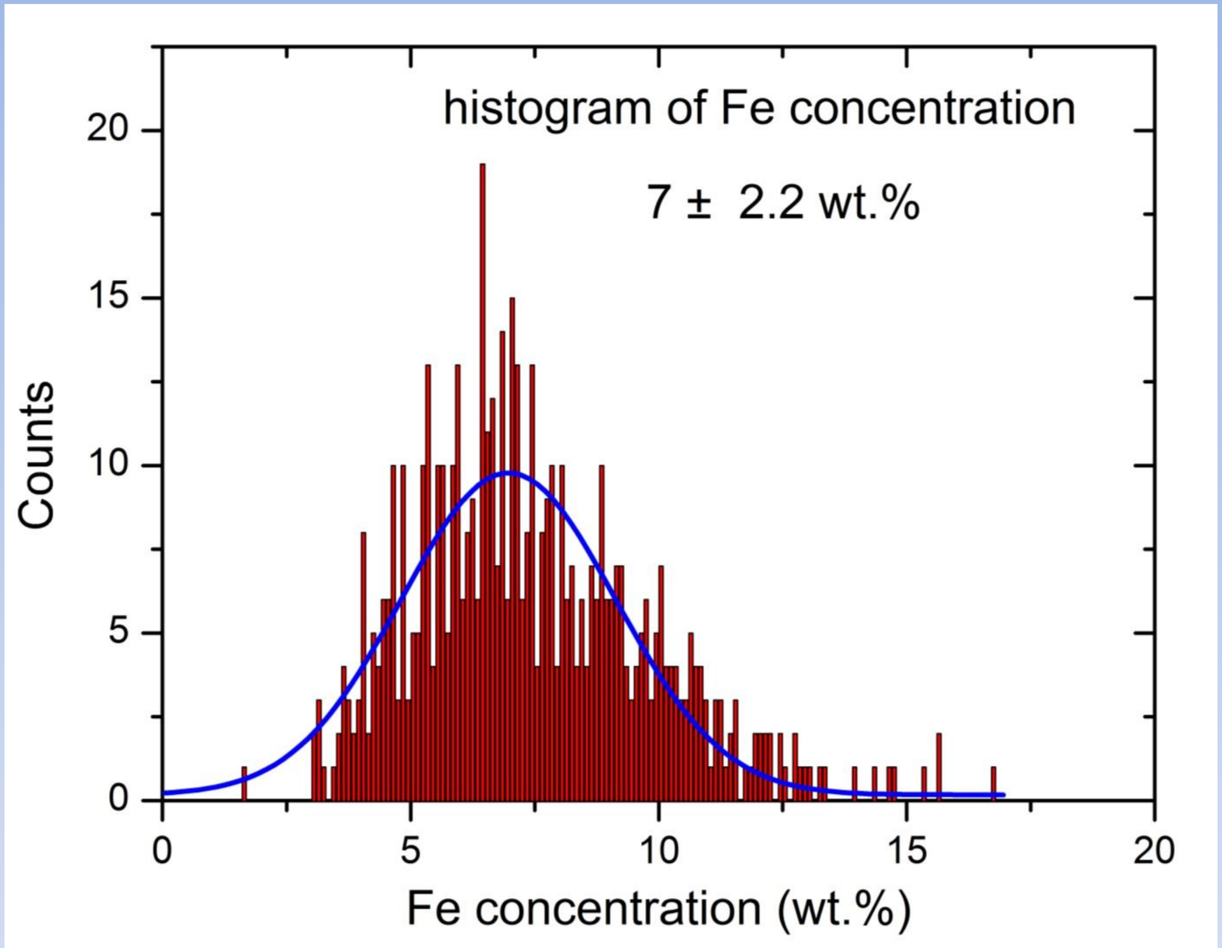
Amphores



Cooking ware

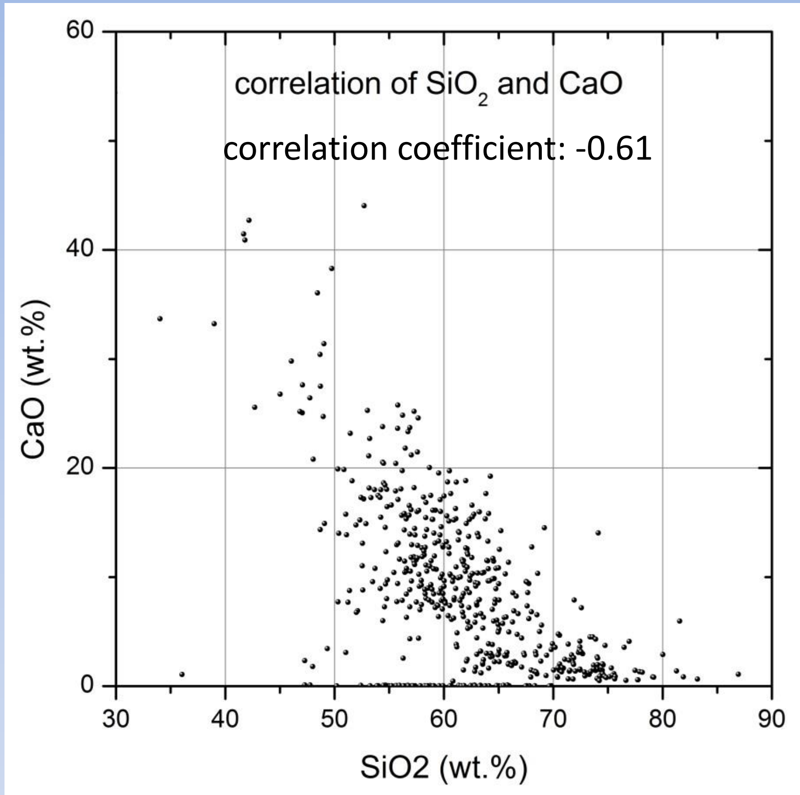


Fe concentration of 550 samples

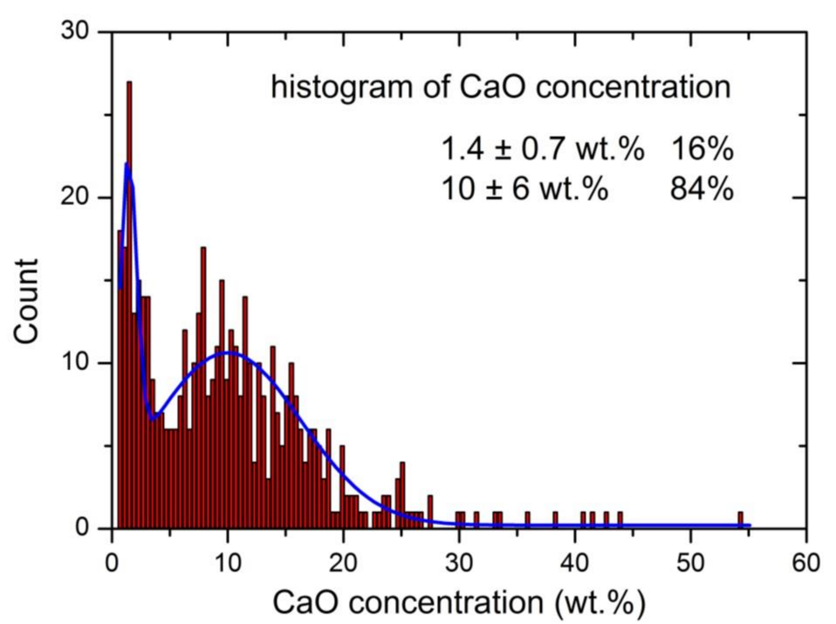


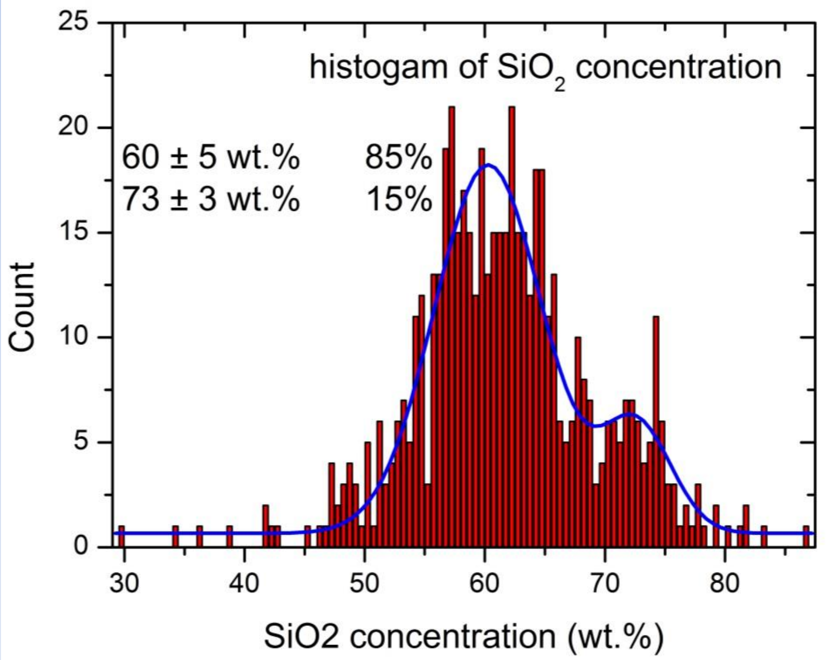
- No significant features regarding the Fe content

Correlation SiO_2 and CaO



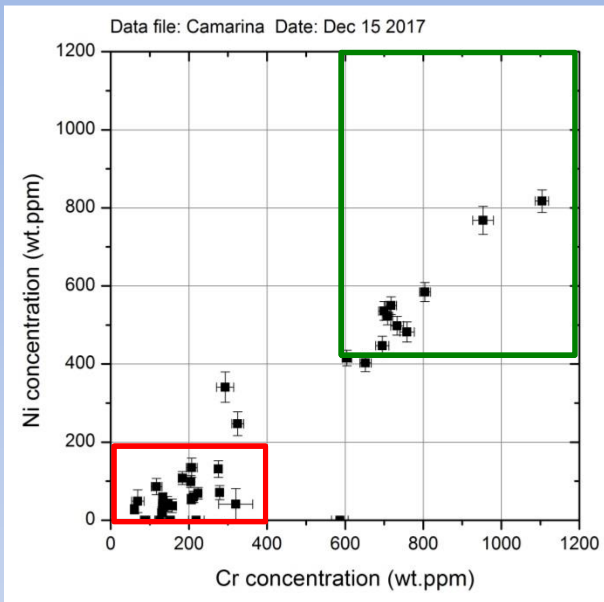
- Clear **anti-correlation** between SiO_2 and CaO content
- Indication of a bimodal distribution

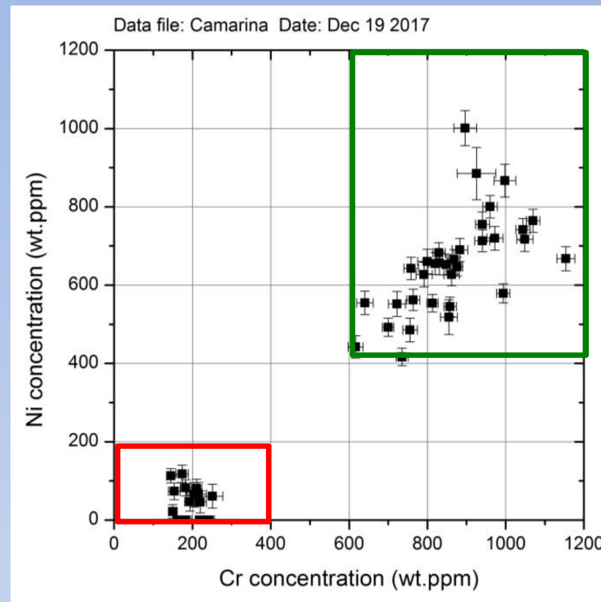


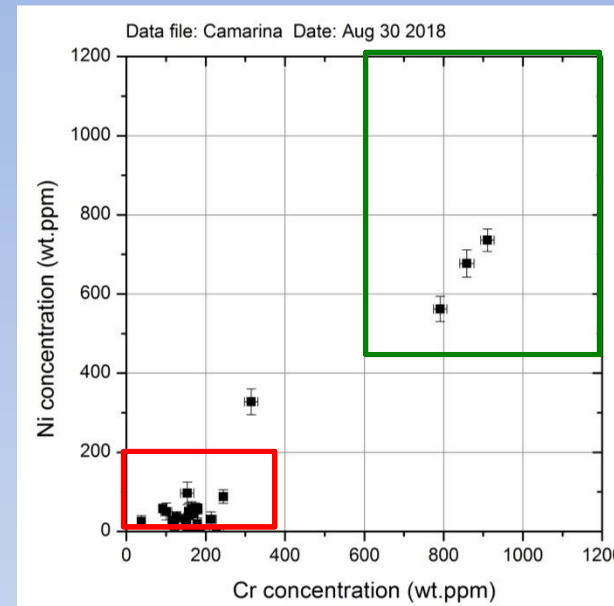


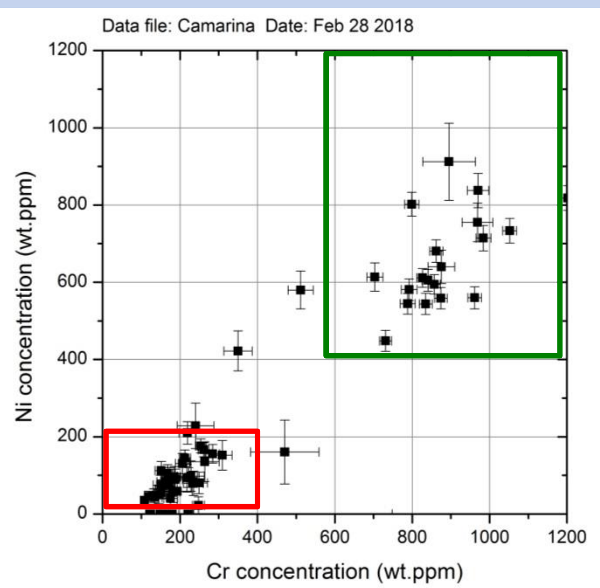
Cr and Ni concentrations

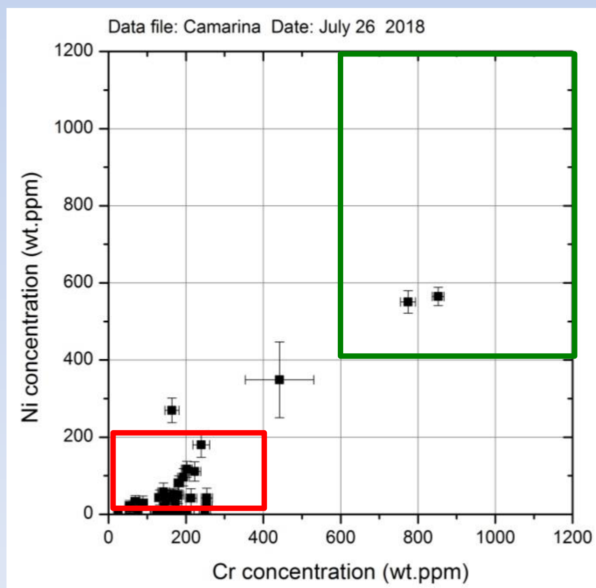
Bimodal distribution of Cr and Ni in Camarina samples

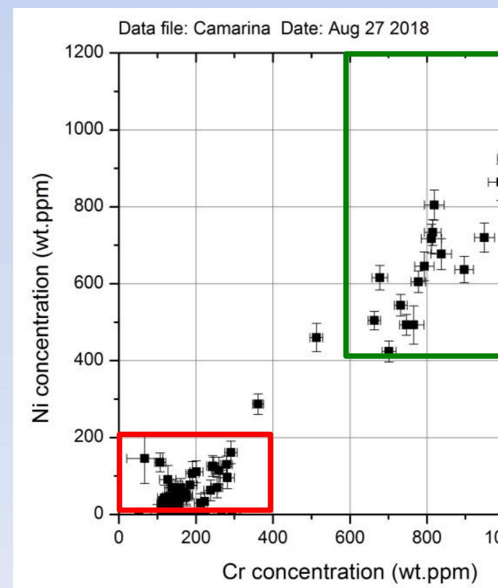






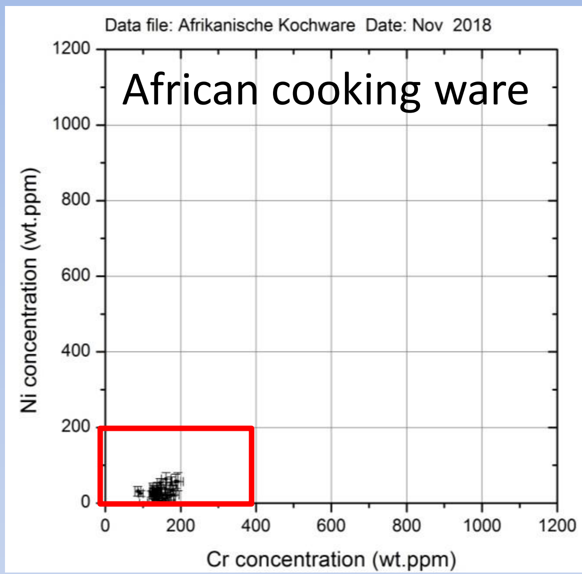


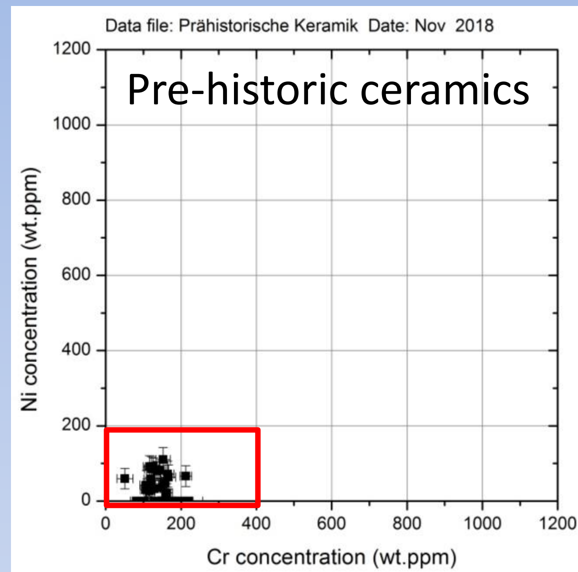


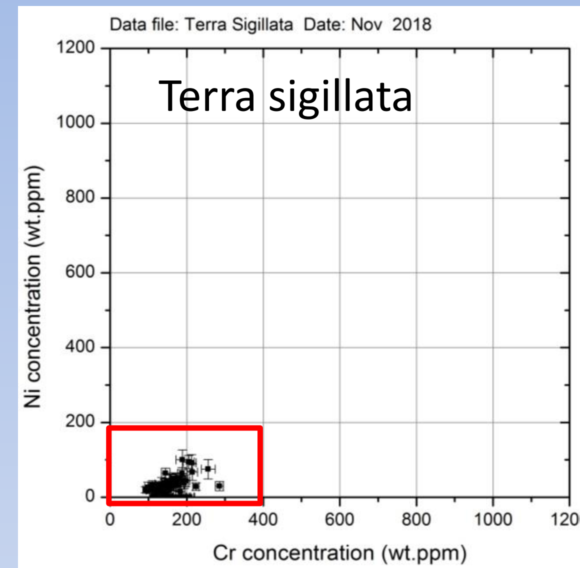


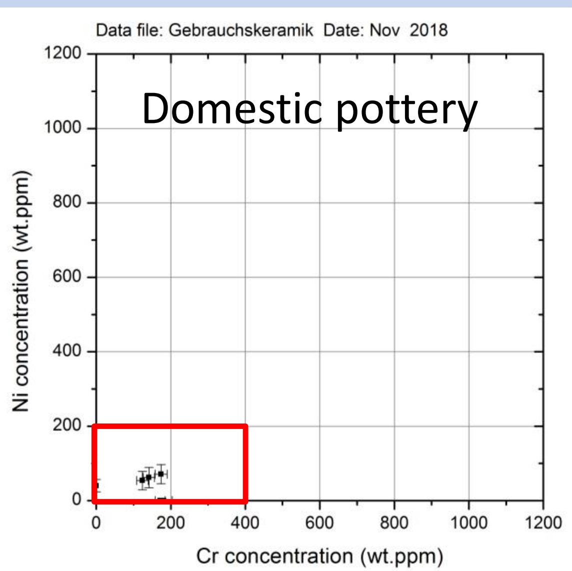
Cr and Ni concentrations

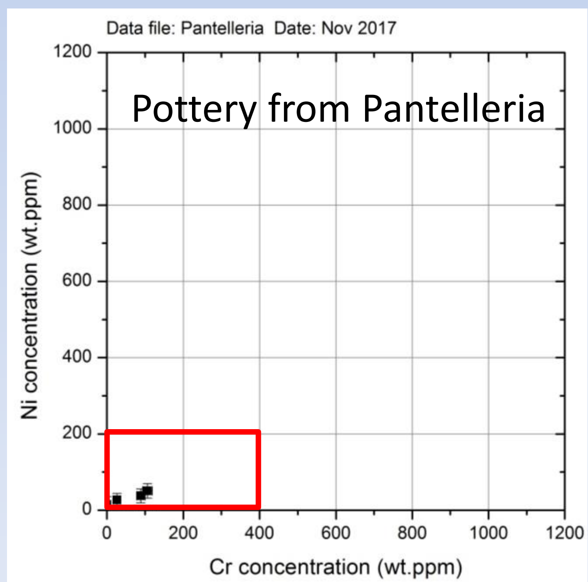
Low concentration of Cr and Ni in most samples Cr < 400 ppm Ni < 200 ppm

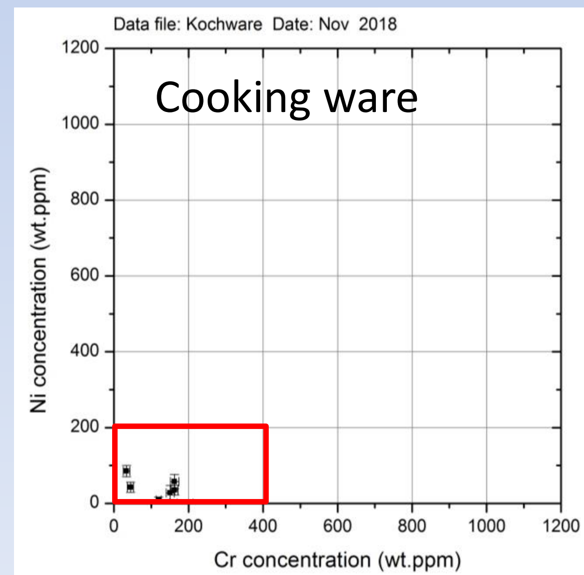








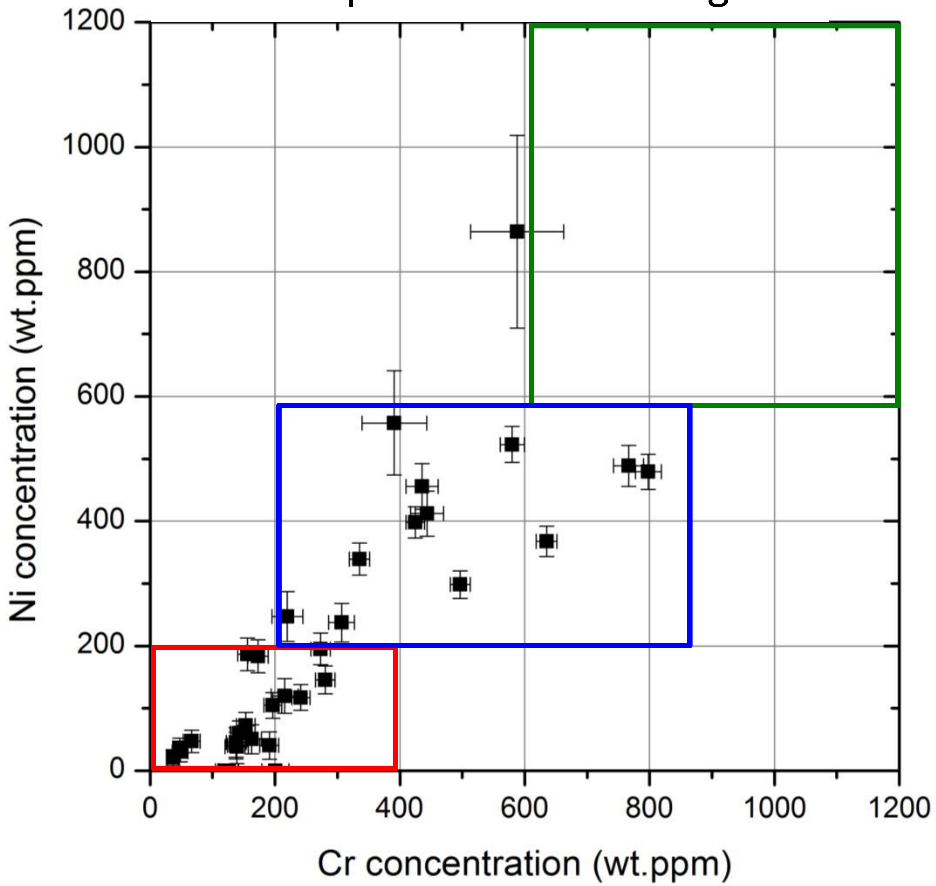




Cr and Ni concentrations

- **Cr and Ni content are usually correlated**
- Only samples from Camarina show high Cr (> 600 ppm) and high Ni (> 600 ppm) content
- Most other samples have low Cr (< 400 ppm) and Löw Ni (< 200 ppm) content
- **Greek black gloss : many samples with medium Cr and Ni**

Greek laquer ware or black gloss

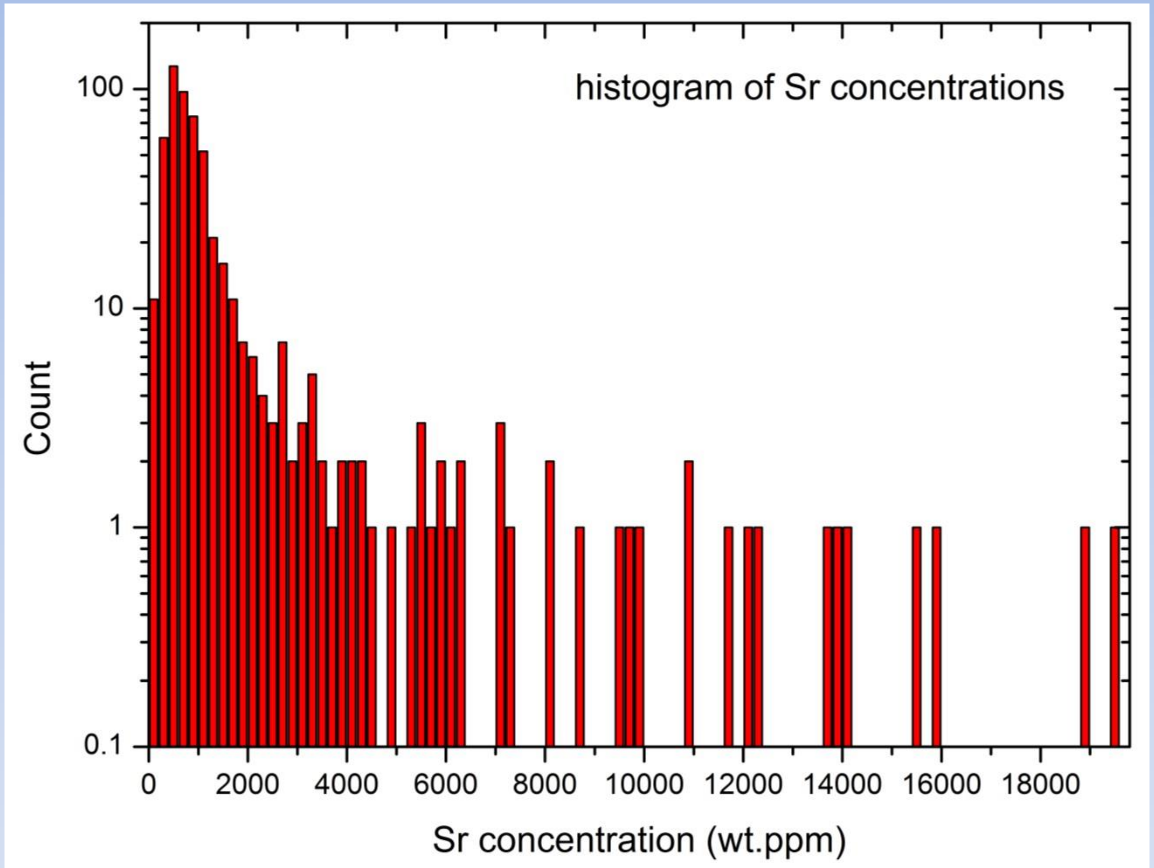


- **No correlations between**
  - Ni-Cu
  - Ni-Mn
  - Cu-Mn
  - Ni-V
  - Mn-Zn

Cr-Ni content may be an indication of the origin of the clay

Sr concentration

- Typically below 0.2 wt.%
- In about 5 % of the samples up to 2 wt.%



- Sr concentration in rocks < 600 ppm
- Sr concentration in soil < 1000 pmm

- Sr containing minerals like
  - Coelestine
  - Strontianite

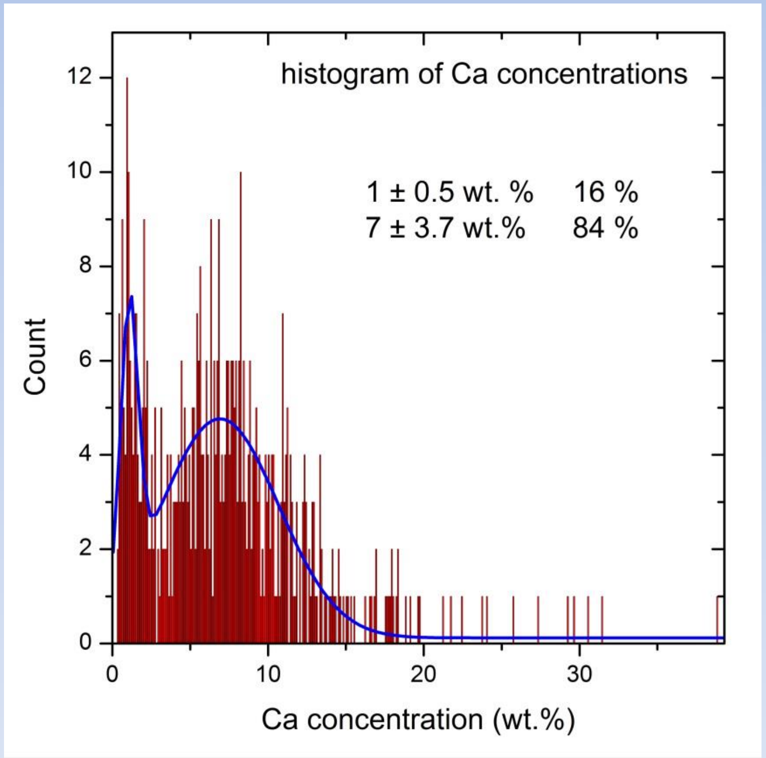
could contribute to higher Sr concentrations

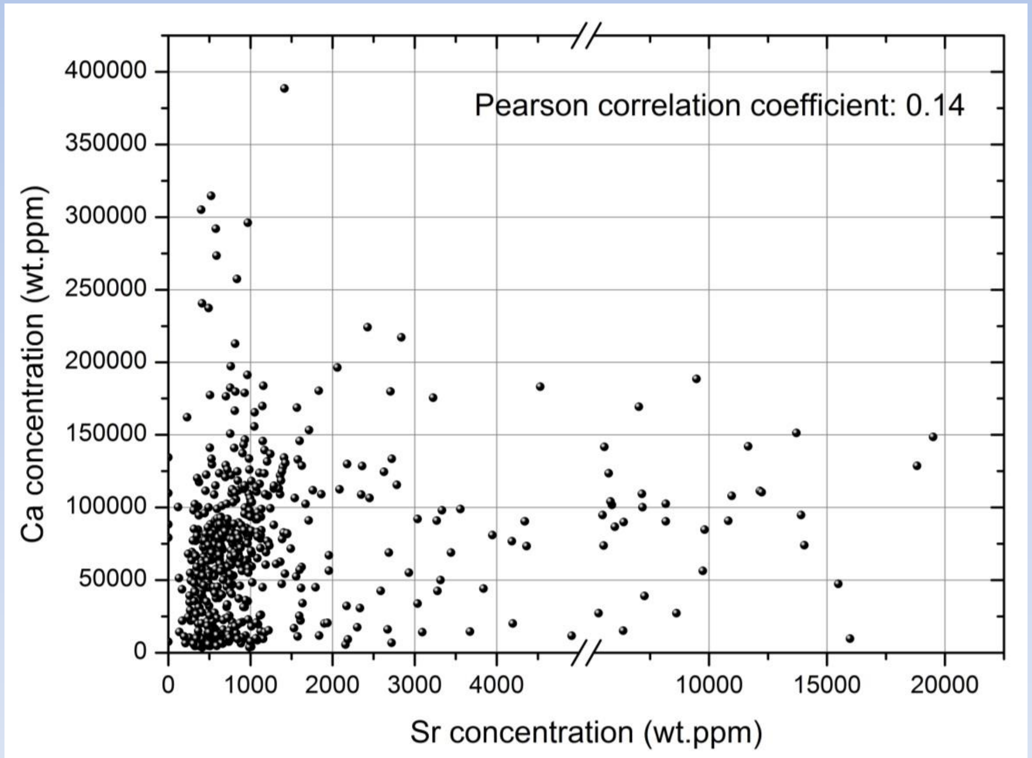
Sr concentration could be an indication of the provenance

Comparison of Sr an Ca concentration

Bi-modal distribution of Ca
- Center at 2 %
- Center at 8 %

High Ca and high Sr content are not correlated





see page 12 , CaO

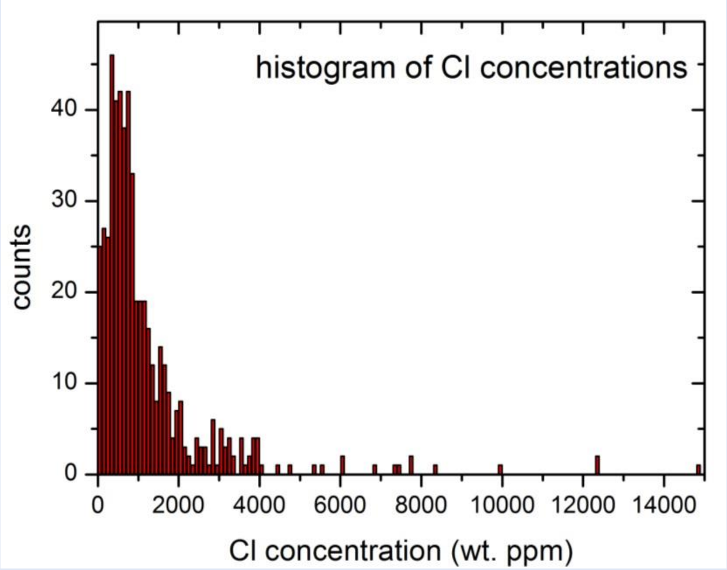
Summary for other elements

Sulfur content > 0.2 wt.% : 65 samples (12%) max. concentration 7 wt.%
Lead content: typical 200 - 400 ppm max. concentration < 2000 ppm
Manganese: typical < 500 ppm; some < 3500 ppm 0.4 %: 2 samples
1 % : 1 sample
Zinc: < 600 ppm 0. 1 %: 1 sample
0.6 % : 1 sample

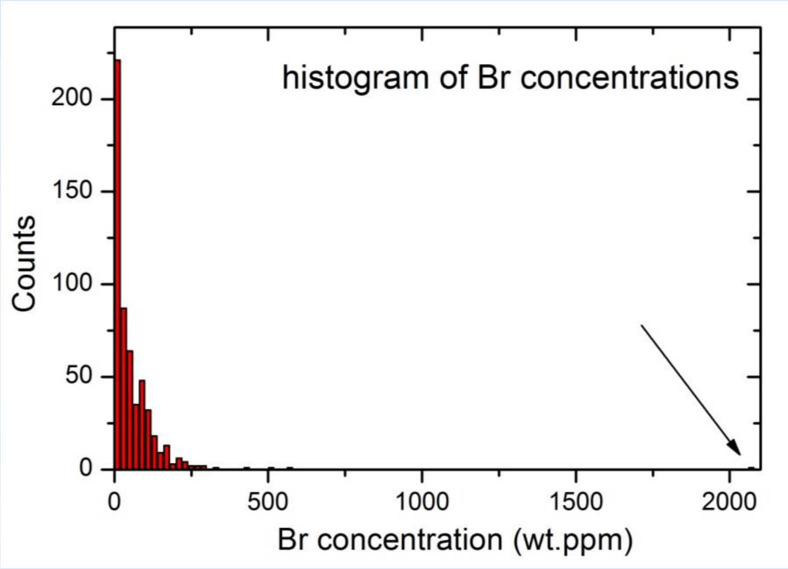
Titanium: 0.6-1.2 wt.% few samples up to 2 wt.%

Bromine: typical 100 ppm, < 300 ppm **2000 ppm: 1 sample**

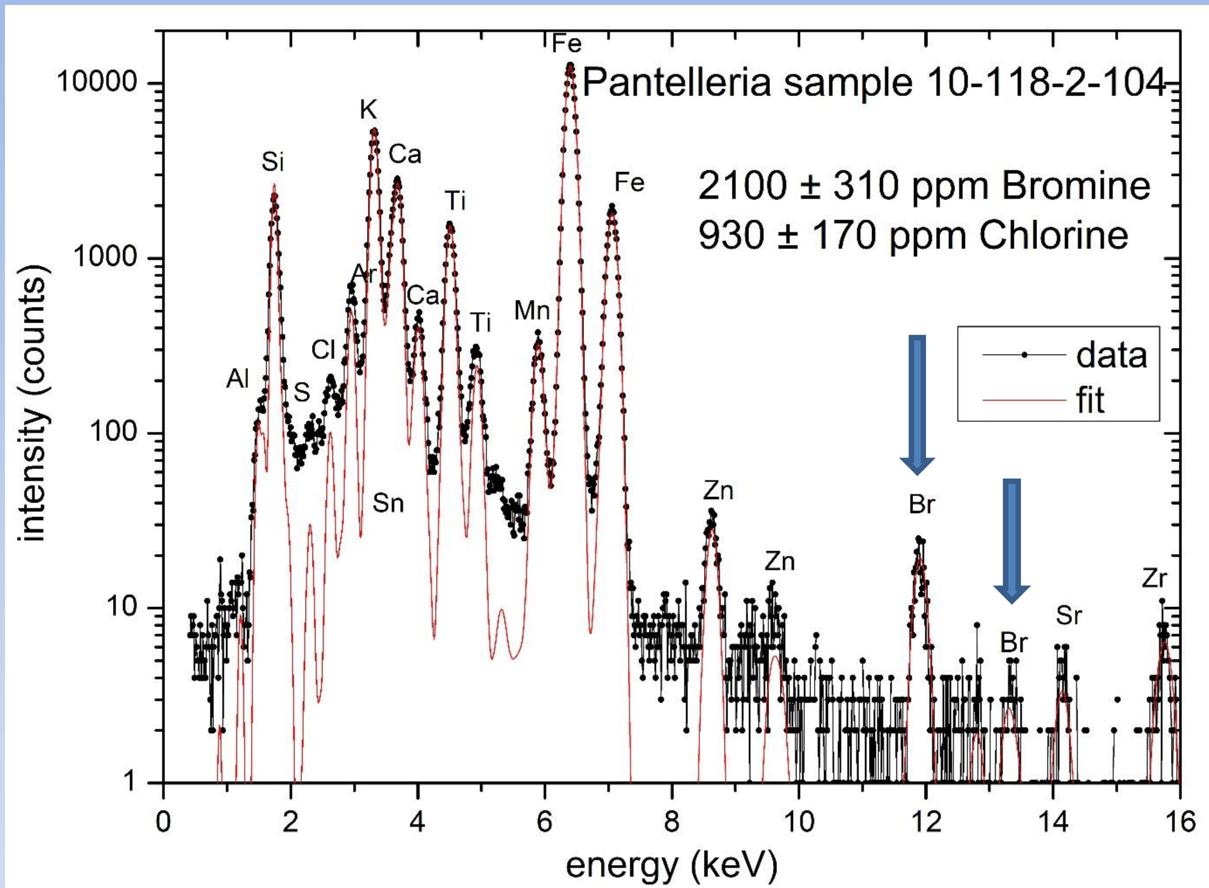
Chlorine:



Bromine:



1 sample out of 550 has an unusual high Br content of 0.2 wt.%



- Ocean 65 ppm Br
- Ocean 2.1 wt.% Cl
- Br:Cl ≈ 1:660

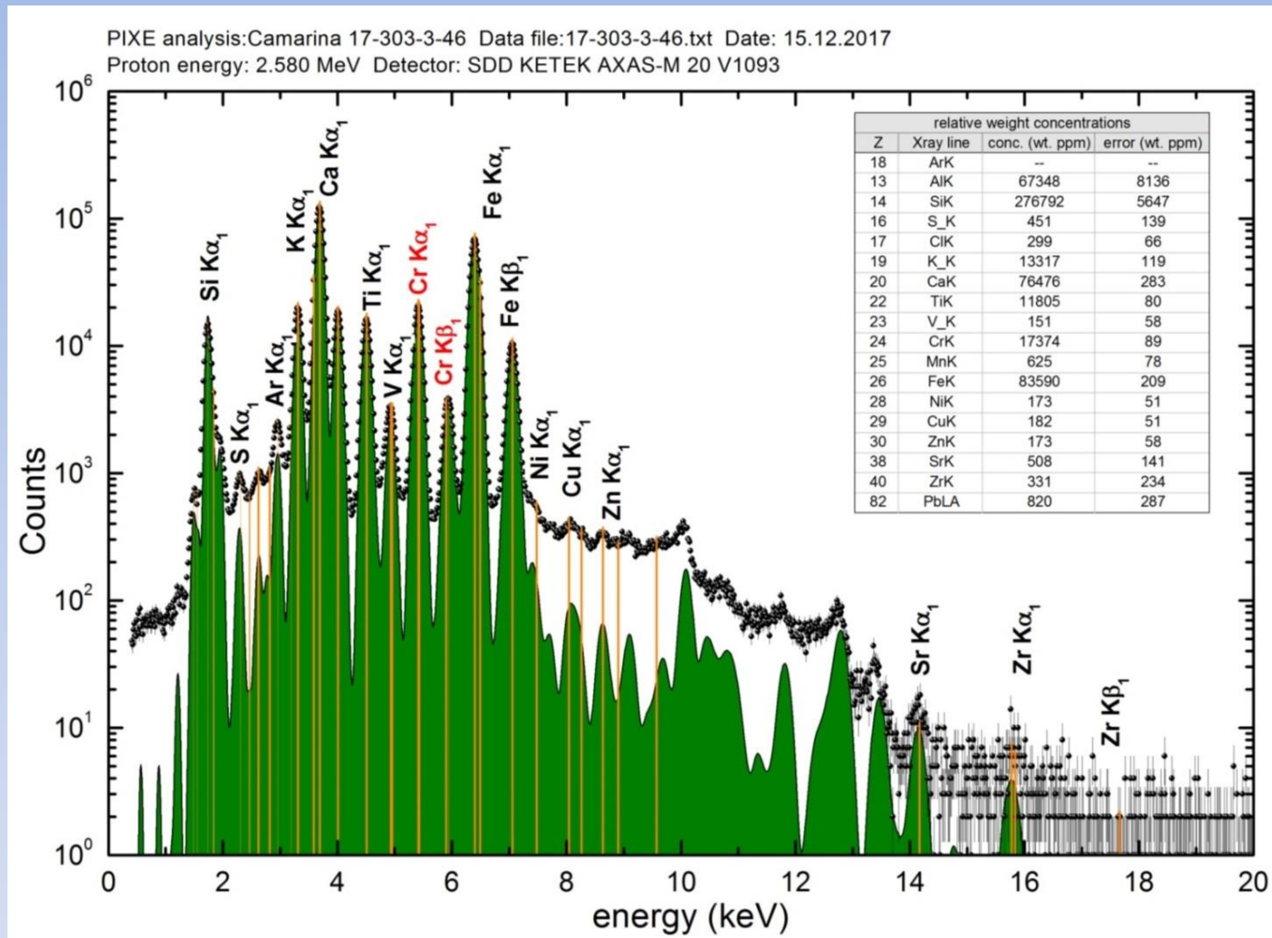
Possible origin of high Br concentration:

- Tyrian purple, a reddish purple natural dye
- The main chemical is **6,6′-dibromoindigo**.
- Production from sea snails
- Pottery was possibly exposed to Tyrian purple dye ?

- purple-dyed textiles became status symbols, whose use was restricted by sumptuary laws

1 sample out of 550 has an unusual high Cr content of 1.7 wt.%

Typical Cr concentration < 1200 ppm



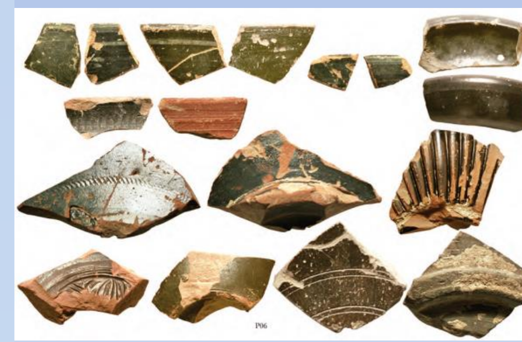
relative weight concentrations			
Z	Xray line	conc. (wt. ppm)	error (wt. ppm)
18	ArK	--	--
13	AlK	67348	8136
14	SiK	276792	5647
16	S_K	451	139
17	ClK	299	66
19	K_K	13317	119
20	CaK	76476	283
22	TiK	11805	80
23	V_K	151	58
24	CrK	17374	89
25	MnK	625	78
26	FeK	83590	209
28	NiK	173	51
29	CuK	182	51
30	ZnK	173	58
38	SrK	508	141
40	ZrK	331	234
82	PbLA	820	287

Possible origin ?

- Cr in soil and groundwater has been linked to geogenic processes, namely, weathering of ultramafic rocks (Mg-Fe minerals, serpentine) , M. Chrysochoou, Curr. Poll. Rep. 2 (2016) 224

Summary

- **Tiny fragments, which usually are being thrown away, get a high value as samples, as they can be used with local permission**
- **PIXE analyses of 1mm^2 spot size with 2.5 MeV external proton beam, 550 samples were analyzed**
- **Calibration of setup using Au/Pt/Ta-foils and „Nordic gold“**
- **SiO_2 – Al_2O_3 – CaO composition indicates different types of clay, Si and Ca content are anti-correlated**
- **Cr and Ni are correlated and show bimodal or trimodal distributions**
- **Often unusual high Sr concentrations**
- **One sample with very high Br content identified**
- **One sample with very high Cr content identified**



Compare with : G. Barone et al. , Archaeometry 56 (2014) 70 XRF
G. Barone, et al. Per. Mineral 73 (2003) 43 XRF , ICP-MS
G. Montana et al., Archaeometry 49 (2007) 455 XRF

Outlook

Comparison with samples of known provenance

- Ceramics from Athens
- Ceramics from Corfu
- Ceramics from Olympia
- Ceramics from Gela
- Ceramics from Tarent