Application to Cultural Heritage II- INES - GEM - ENGINX @ISIS

Antonella Scherillo

ISIS facility, STFC, UK

CNR-IPCF, Messina, Italy

30 April – 9 May 2014 XII School on Neutron Scattering (SoNS) "Francesco Paolo Ricci"

Presentation Outline:

Instrument for archaelogical science operational at ISIS :

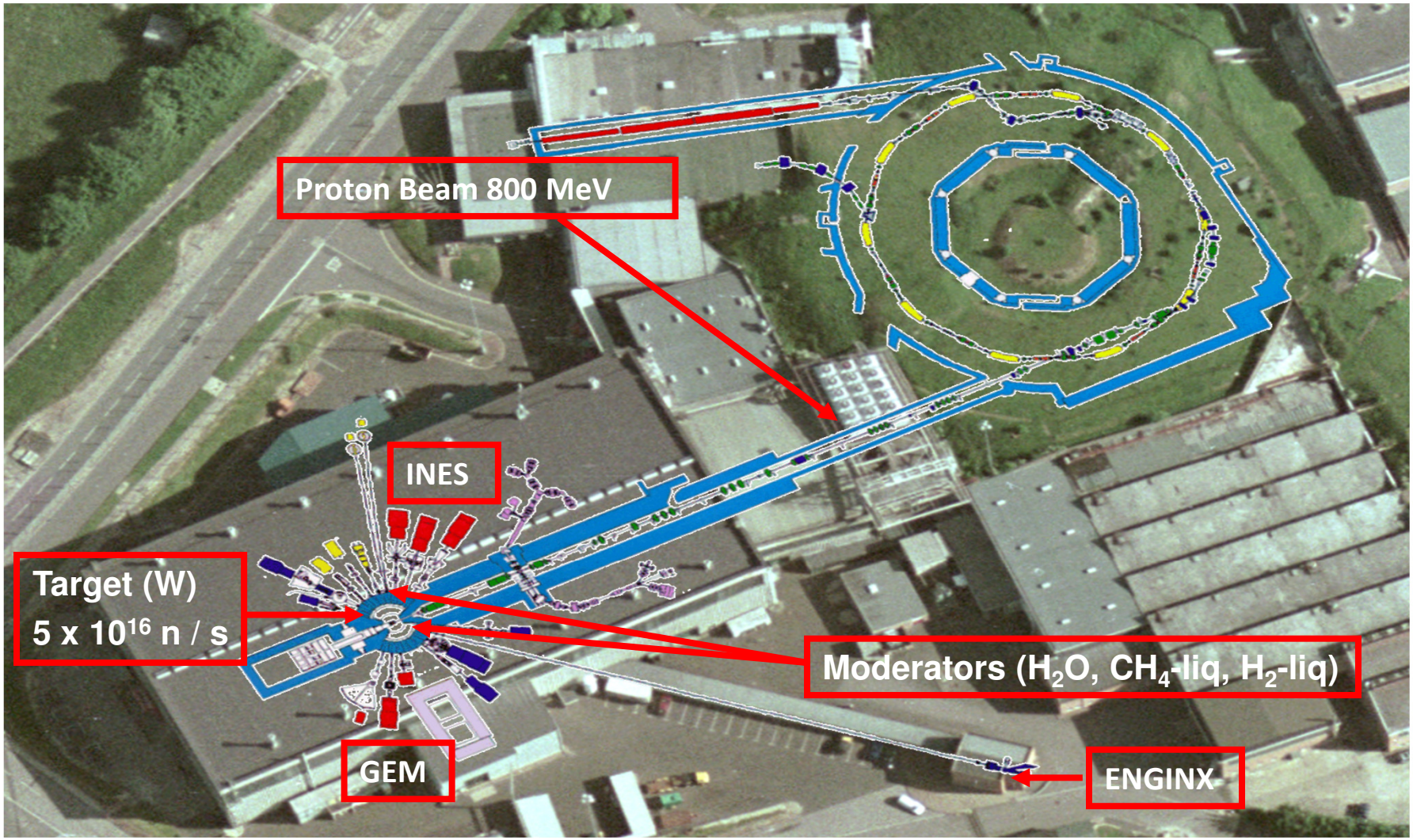
- **INES – powder diffractometer**
- **EnginX – strain scanner**
- **GEM – powder diffractomenter, texture measurements**

Italian Neutron Experimental Station INES@ISIS

Instrument director: Dr. Cirino Vasi, CNR Italy
Instrument scientist: Dr. Antonella Scherillo, CNR, Italy - STFC, UK

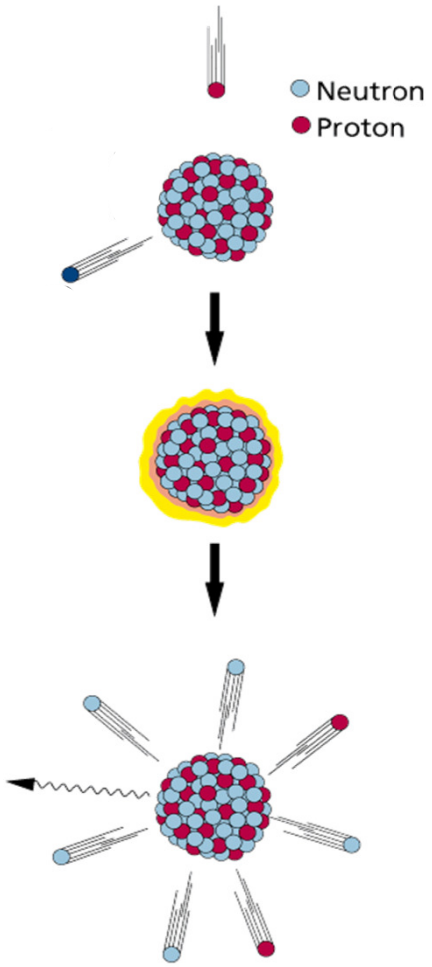
- **Ines is a powder diffractometer built and managed by CNR Italy, operating at the ISIS spallation source, UK**
- **INES became fully operational in 2007, since then it is open to proposal from international community**
- **Your proposals are welcome!**

The ISIS Spallation Neutron Source TS1



The ISIS Spallation Neutron Source

- Neutron at ISIS are produced by means of spallation reaction
- An 800 MeV proton accelerator produces intense pulses of protons 50 times a second. 4 pulses go to TS1, one to TS2
- The tungsten target is bombarded with these pulses of high energy protons. This gives an extremely intense neutron pulse
- The neutrons are slowed to speeds useful for condensed matter research by an array of hydrogenous moderators around the target
- They are then directed to a suite of neutron instruments, each optimised to explore different properties of materials



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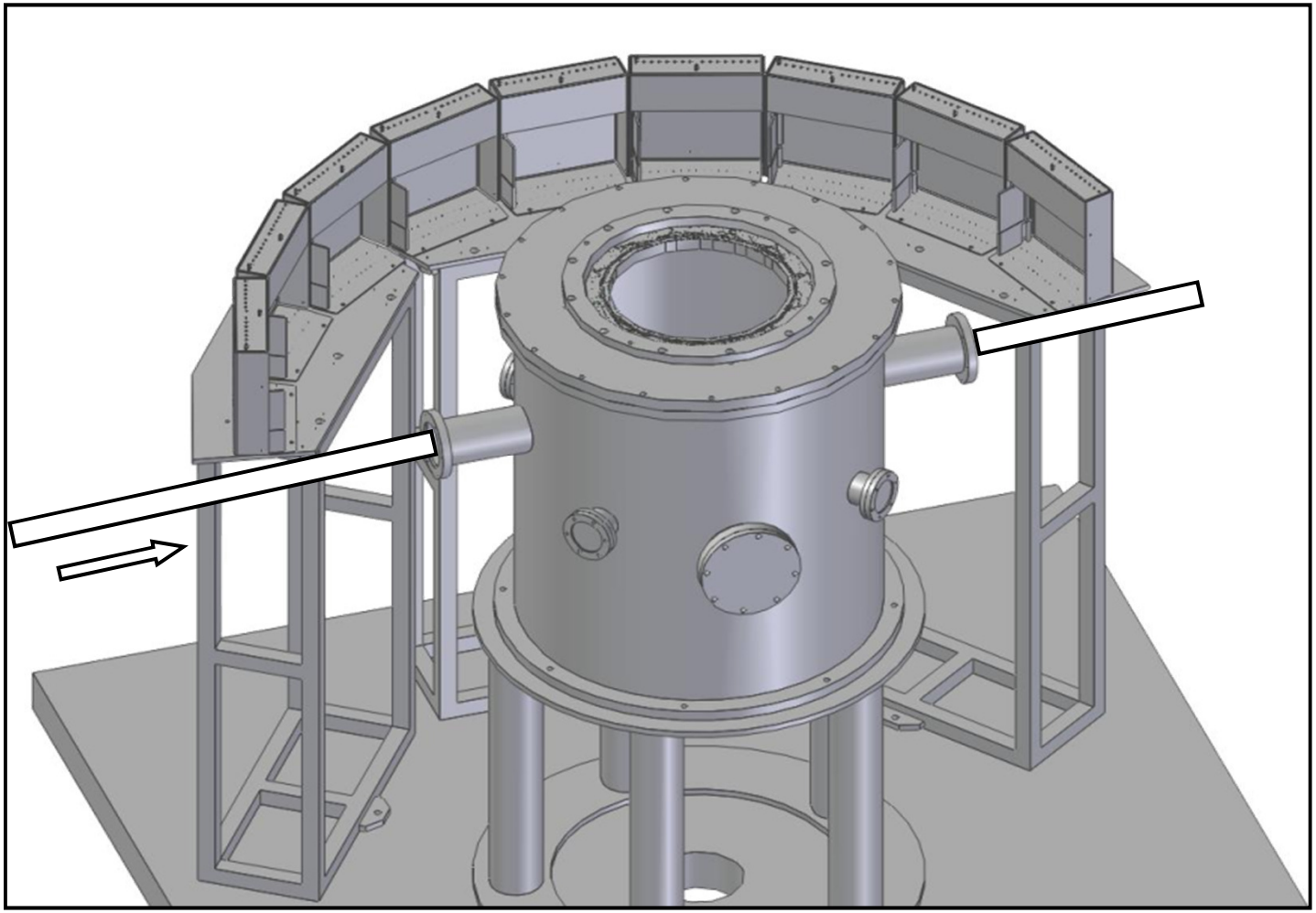

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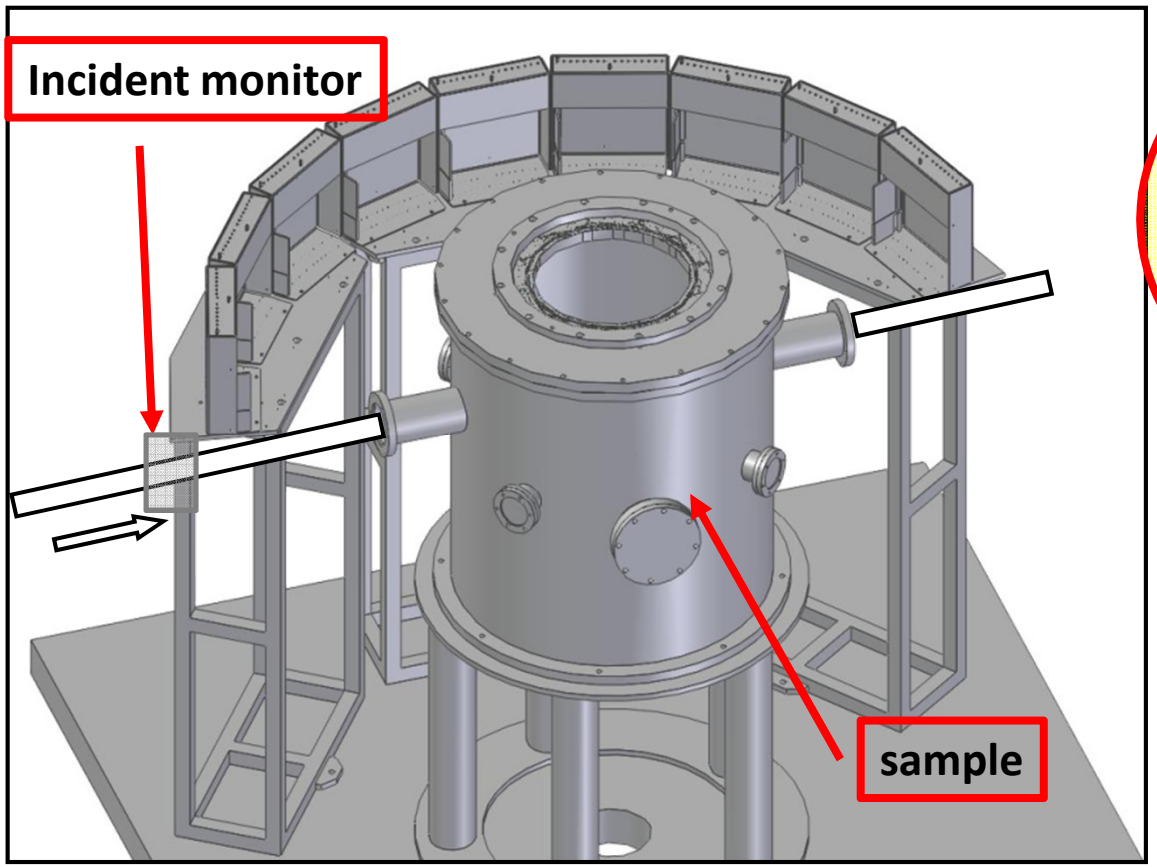

Italian Neutron Experimental Station

- Large sample holder tank (1 m^3)
- 144 diffraction detectors ^3He
- 9 banks
- d-spacing: 0.4-12.0 Å
- High resolution: 0.10% backscattering
- High signal to noise ratio
- Beam size: 30x30mm
- Jaws to shape the beam: min 2x2mm
- Laser pointer to align the sample
- Radiography apparatus to align and scan through the sample
- Sample changer and XY table
- NRCA - YAP detector

Italian Neutron Experimental Station
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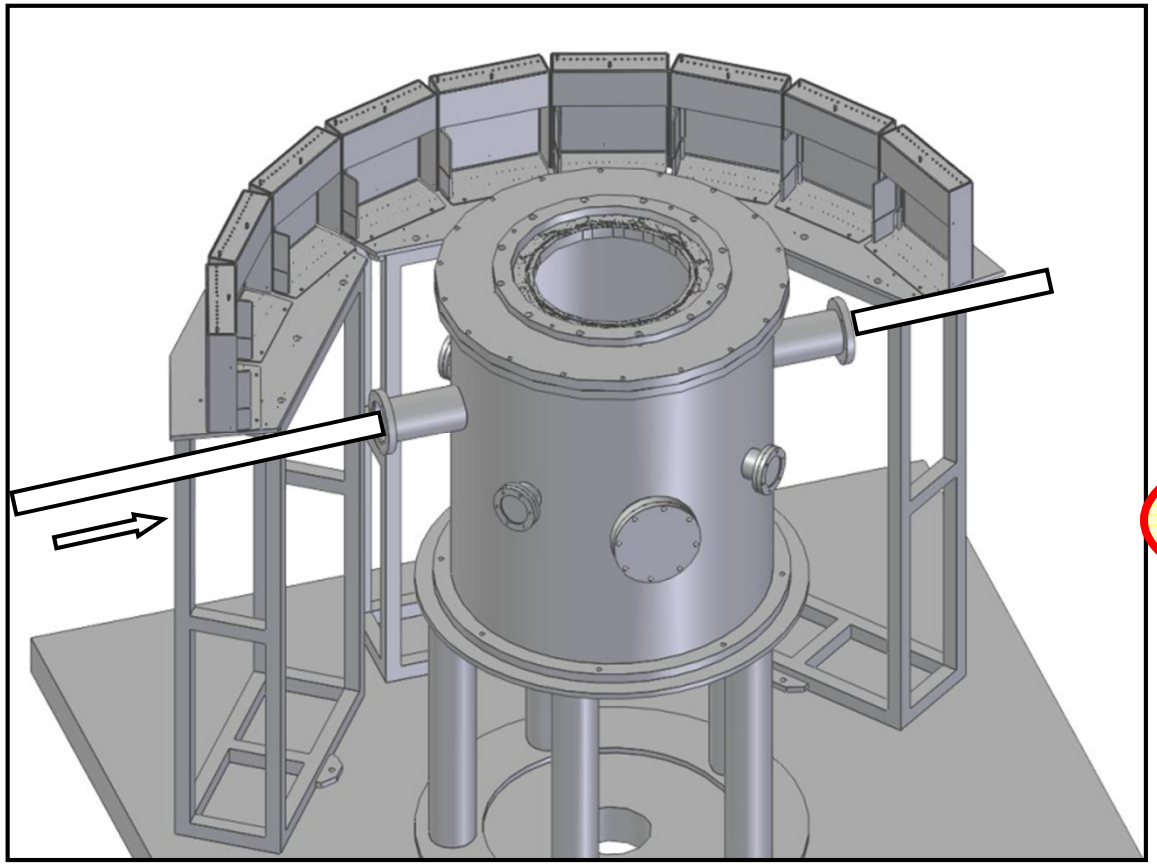

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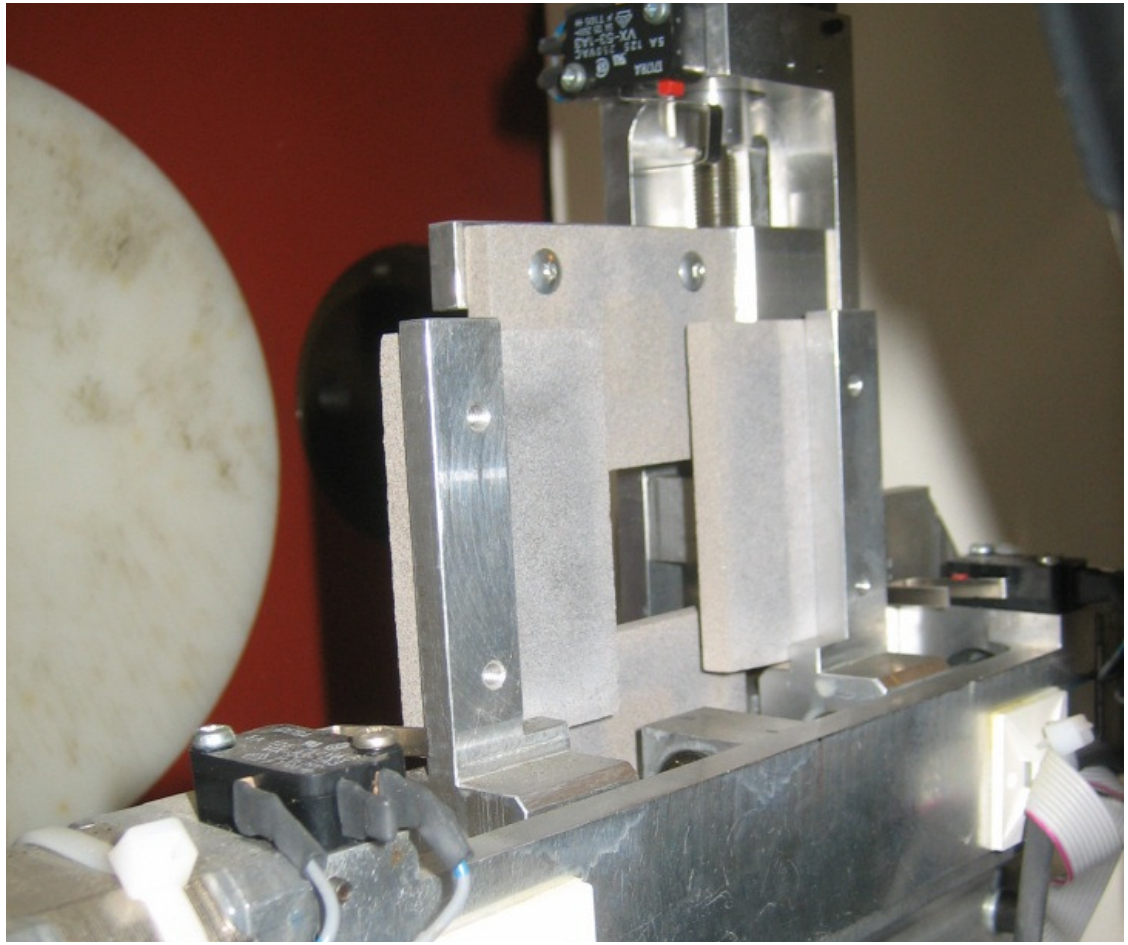

JAWS: neutron absorbing material to shape the beam min 2X2 mm, max 30X30mm

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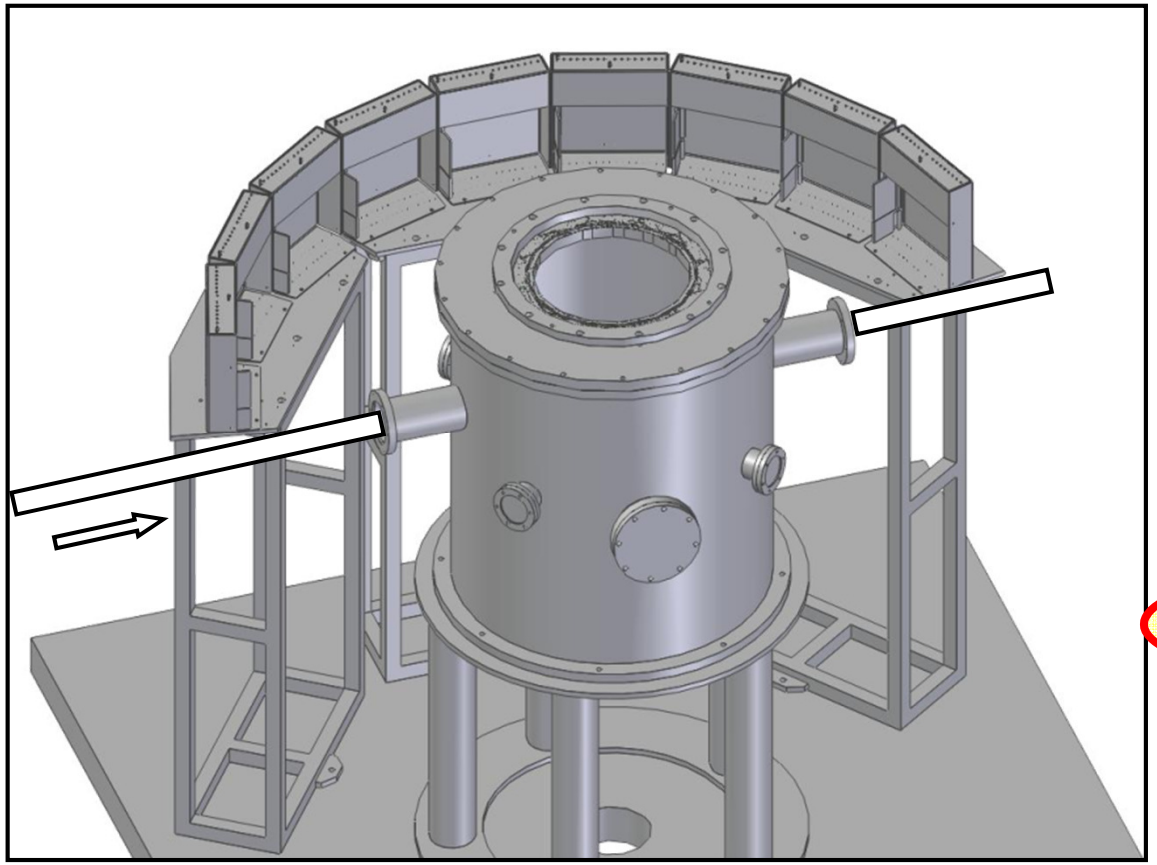

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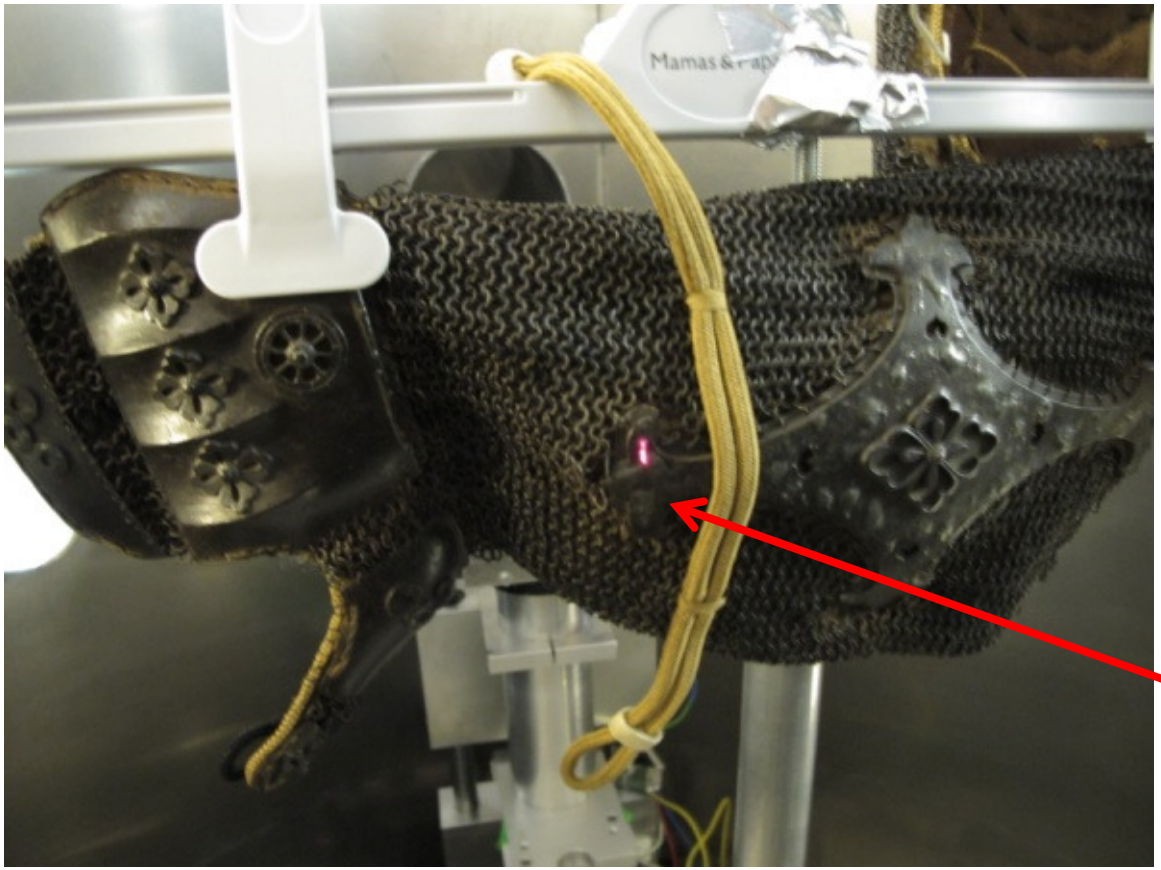

Laser pointer

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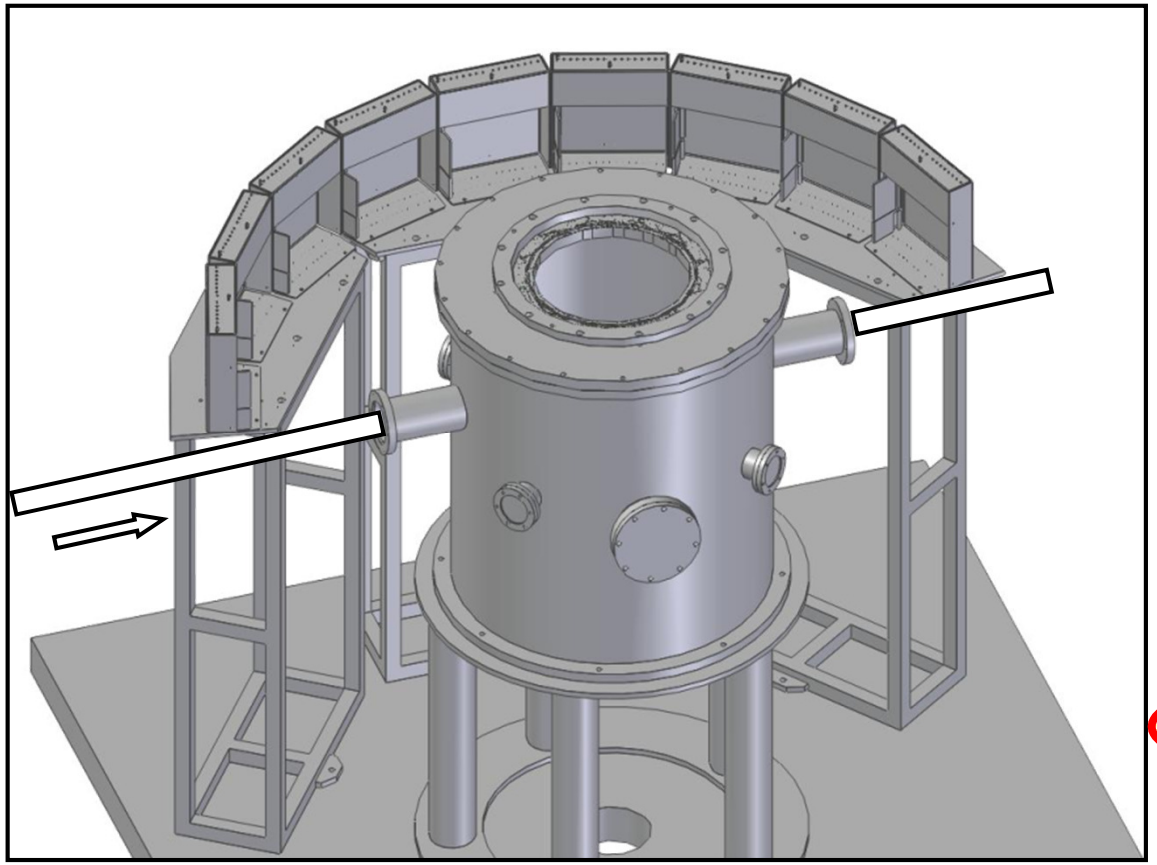

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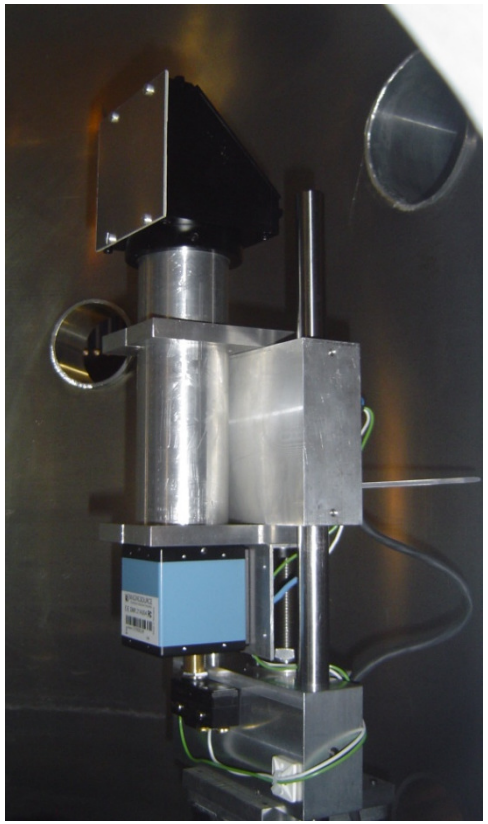

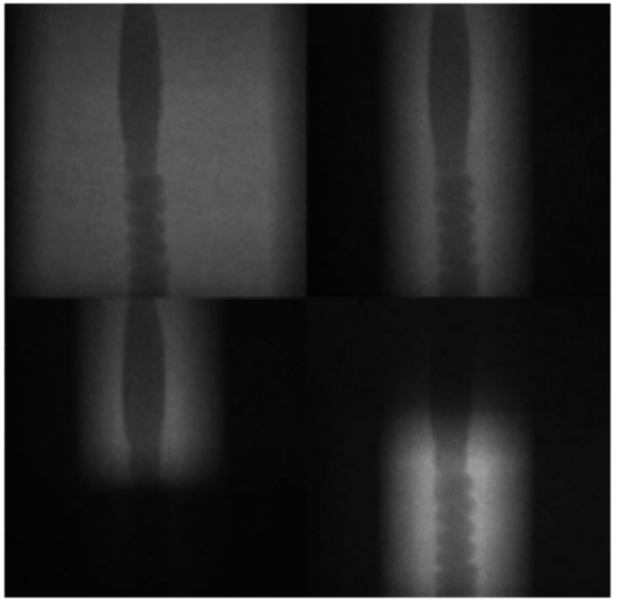

Looking at the image from the camera it is possible to close the jaws to select the desired volume to measure

Neutron camera is made by a scintillator foil (ZnS(Ag)) to convert neutron into light. The light is detected by a CCD camera.

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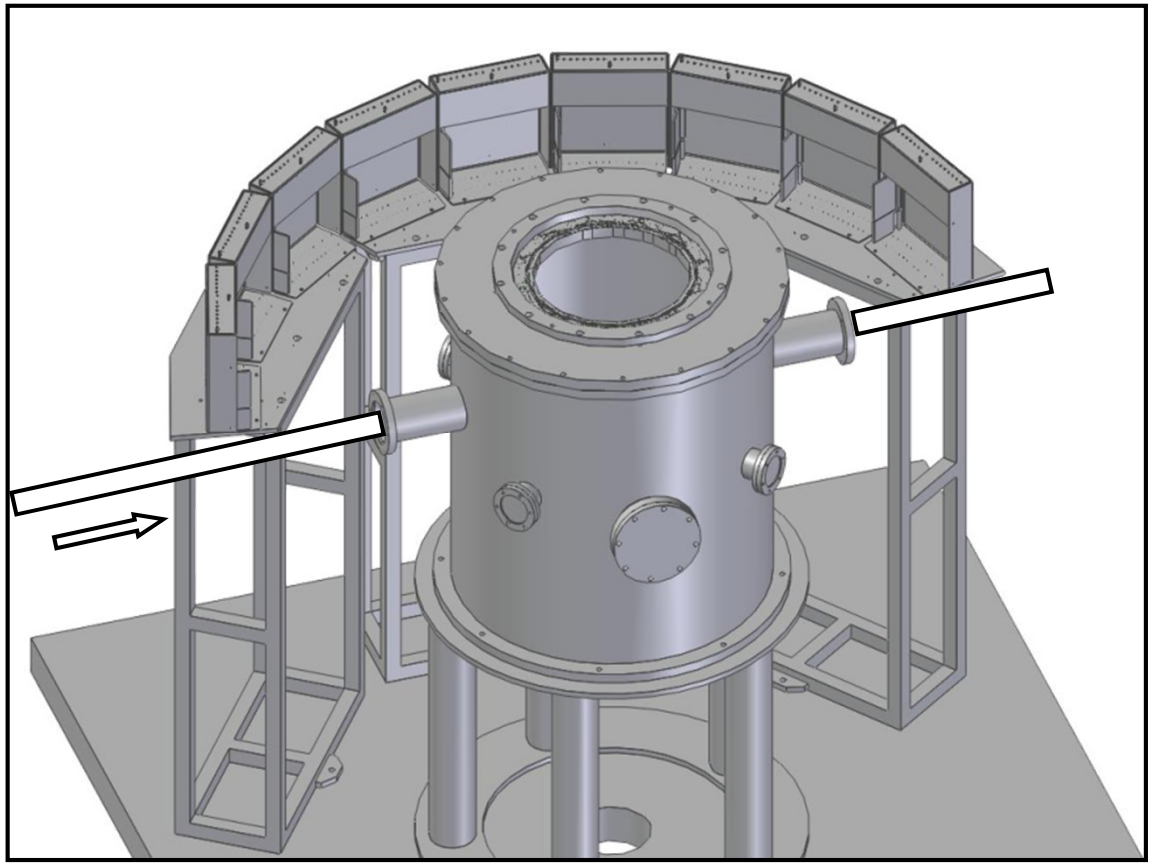

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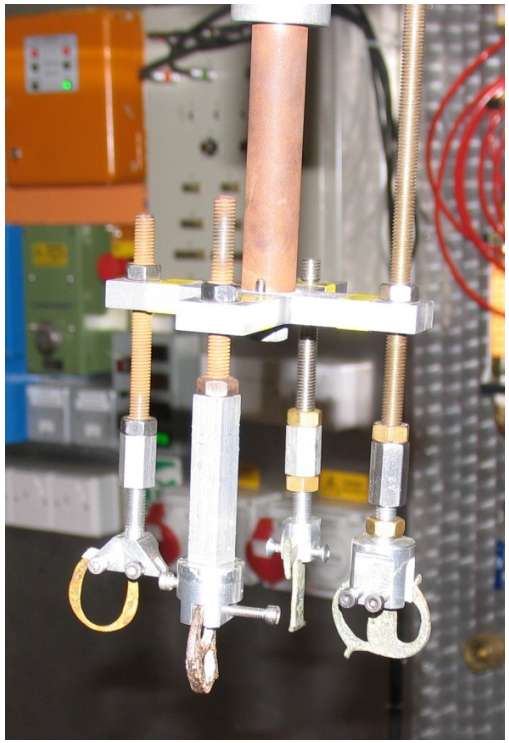
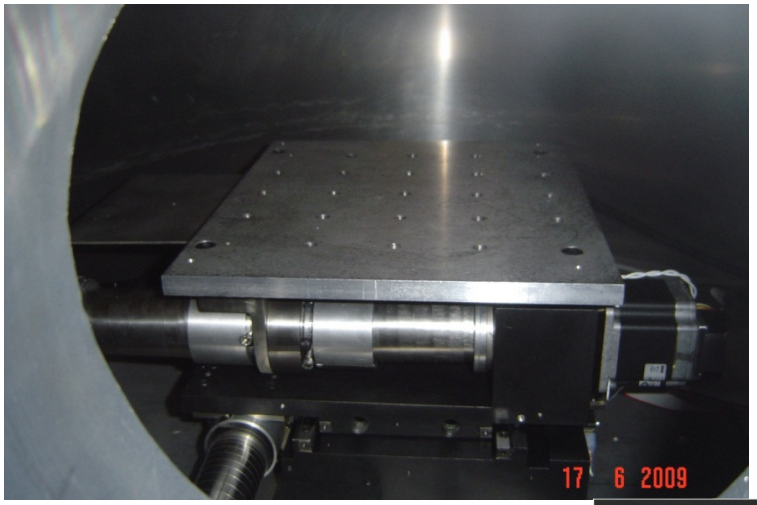
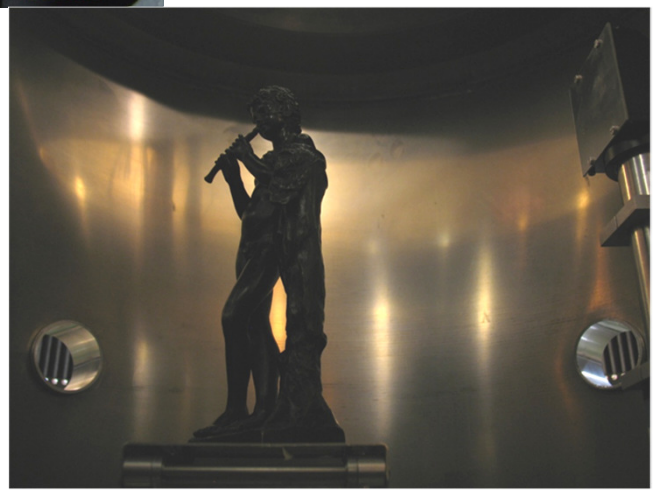


Sample changer



XY table



Statue on XY table

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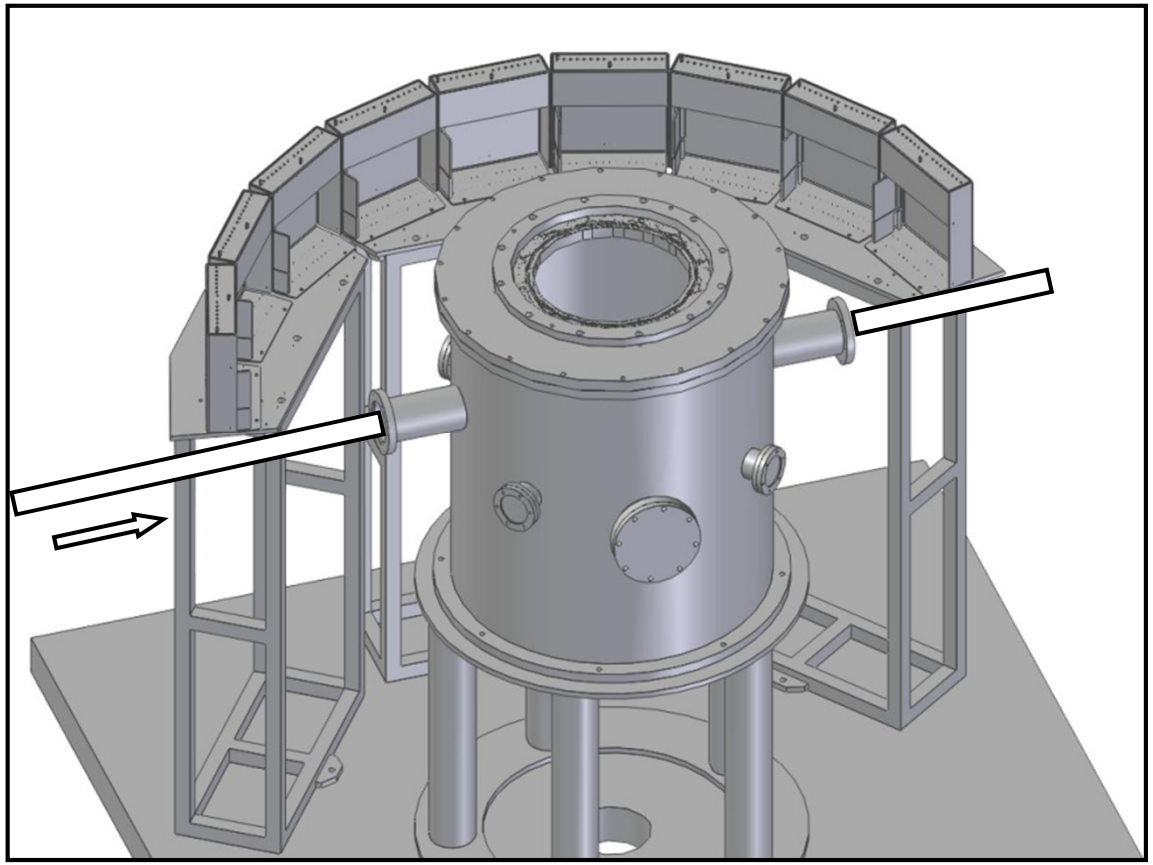

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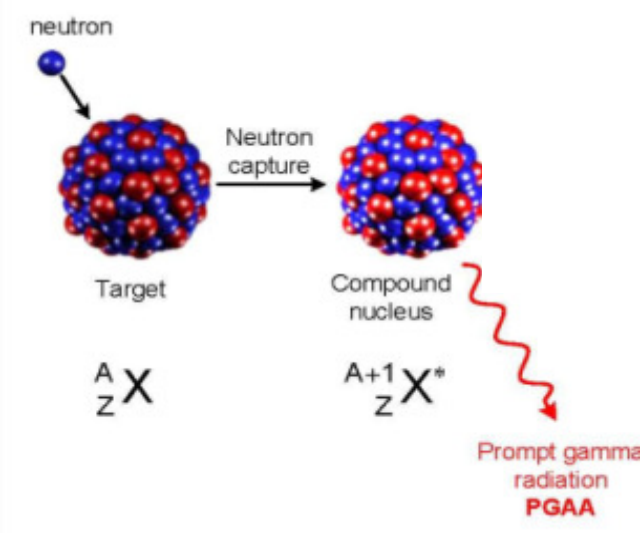
Neutron Resonance Capture Analysis

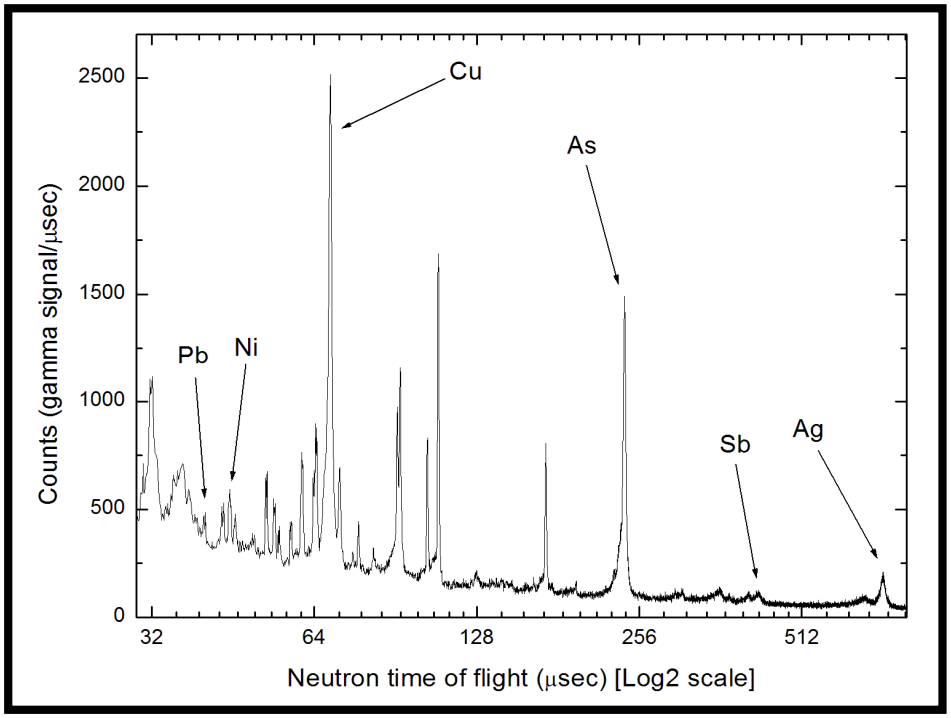


$$n(E) + X_{A,Z} = X^{*}_{A+1,Z}$$

- Nuclear resonances are related with the high density of accessible states for the coumpound nucleus, after neutron capture. Usually they occur at the energy of the epithermal neutron present in the beam
- When a neutron is captured by a nucleus, the excited compound nucleus promptly decay into a more stable state. The time between T_0 (neutron production in the target) and T_γ, the time of the arrival of the γ–ray on the YAP detector is the ToF (energy) of the neutron responsible of the resonance
- Resonance energies are characteristic of the nuclei, so we can identify the components of our sample

Neutron Resonance Capture Analysis

- We can have detailed information on the composition of our sample
- It is isotopic selective



- At present we can have only qualitative (semi-quantitative) information on the atoms in our sample

ToF -ND for Archaeometry

What can be achieved in archaeometry by ToF - Neutron Diffraction measurement?

- **Determine the wt% of crystal phases present in the sample**
- **Alloys composition (elements wt%)**
- **Texture (preferred cristallites orientation)**
- **Cristallite size**
- **Residual stress**

Eneolithic artefact @INES

E. Barzagli *et al*, AIAR 2012

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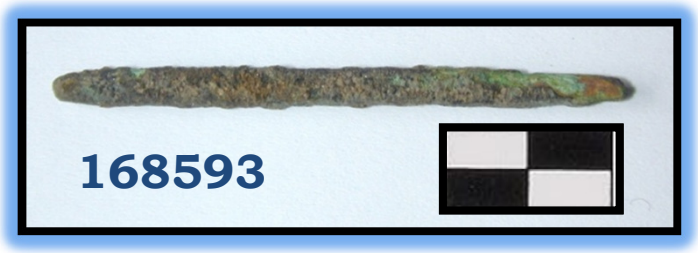
Eneolithic artefact @INES

Idea behind measurements:

- Non destructive characterization of eneolithic artefacts (~4000 BC) from Fontino cave
- Different conservation conditions are due to different composition?
- Was As added deliberately or is a remaining of the rocks rich in As used to obtain Cu?

Eneolithic artefact @INES



1 cm=

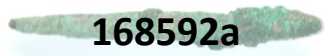
Rivets from Fontino cave

Eneolithic artefact @INES- NRCA

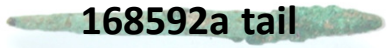
Sample	As	Ag	Sb	Ni	Zn	Pb
 168591 average	maj	min	min	min	trc	---
 168592a head	maj	min	min	min	---	---
 168592a tail	maj	min	min	---	---	---
 168592a average	maj	trc	trc	min	trc	---
 168593 averge	maj	min	min	---	---	---
 168595 average	maj	min	min	min	trc	min

maj: x>1% min: 0.1%<x<1% trc: x<0.1%

Eneolithic artefact @INES- ND

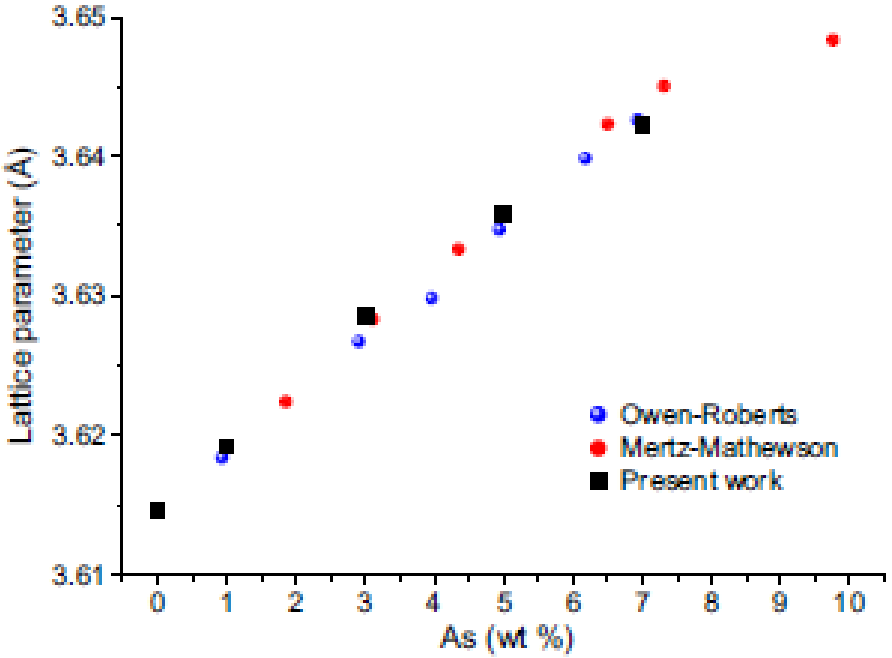
Sample	alpha-copper (wt%)	Lead (wt%)	Cuprite Cu_2O (wt%)	Nantokite CuCl (wt%)	Paratacamite $Cu_2(OH)_3Cl$ (wt%)	Chalcocite Cu_2S (wt%)
 168591 average	96.2±0.1		3.2±0.1	0.3±0.1		0.3±0.2
 168592a head	74.7±0.1		17.4±0.2	6.7±0.2	0.6±0.1	0.6±0.5
 168592a tail	85.7±0.1		9.9±0.1	3.4±0.1		1.0±0.1
 168592b average	79.6±0.1		15.3±0.2	3.1±0.1		2.0±0.5
 168593 average	75.9±0.1		20.8±0.2	0.7±0.1		2.8±0.5
 168595 average	90.9±0.1	0.7±0.1	6.6±0.1	0.6±0.1		1.2±0.2

Eneolithic artefact @INES- ND

Sample	Phase	Lattice parameter (Å)	Phase composition: equivalent As wt%
 168591average	α-Cu-As	3.620	1.5
 168592a head	α-Cu-As	3.617	1.0
 168592a tail	α-Cu-As	3.617	1.0
 168592b average	α-Cu-As	3.620	1.0
 168593 averge	α-Cu-As	3.630	4.0
 168595 average	α-Cu-As	3.628	3.5

Elemental composition of a single phase metal alloy

Cu, As alloy, typical of Eneolithic age



Lattice parameter determination through Rietveld refinement of samples of known composition allowed us to build a reliable calibration curve.
Now we can derive the As content of our sample mesuring the lattice parameter of Cu phase in our objects!!!!

Cu-As is the only case of non linear relationship between element wt% and lattice parameter, a quadratic term is needed

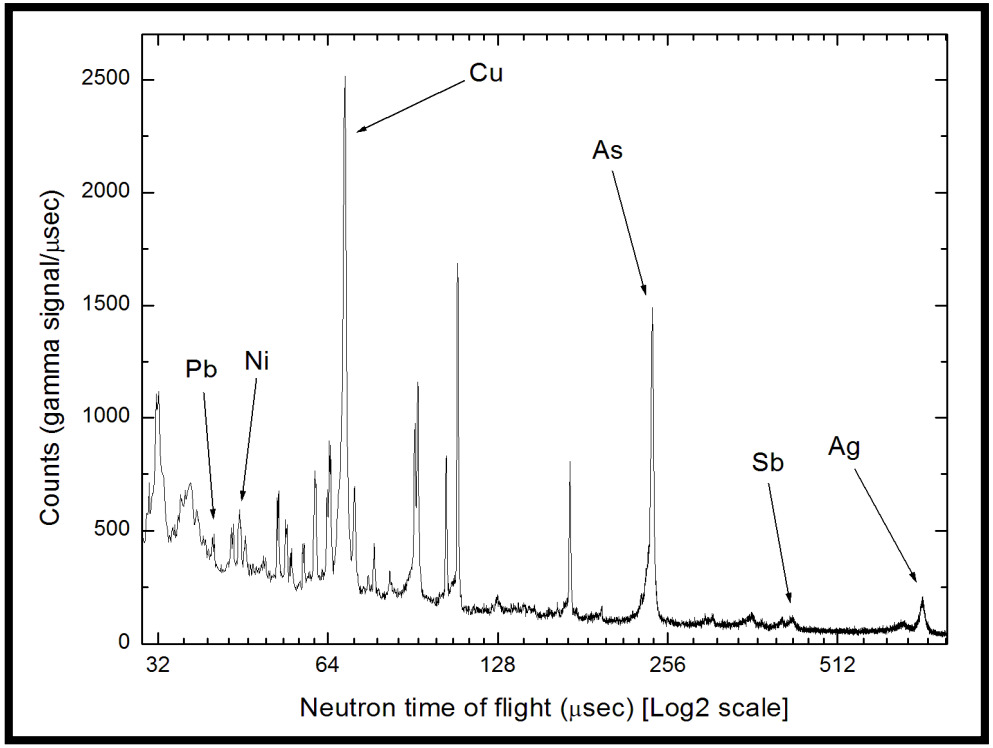
Some conclusions from NRCA+ND

Conclusions obtained by comparison of the peak intensities in the NRCA spectra, and performing the Rietveld refinement:

- **As is present in all the sample**
- **Cu_2S is present in all the samples**

} **The ore used to obtain the copper was copper sulphide, rich in As**

- **In NRCA spectra, where Ag peak is high, As peak is low (sample 168592a) and viceversa. Sample 168592a was made with a ore containing relatively high amount of Ag and low amount of As, whereas for the others is the contrary**



Some conclusions from NRCA+ND

- Only one sample contains lead. Too low concentration to assume a deliberate addition
- Even in the same sample, conservation condition are different, therefore even small change in the environment can cause big difference in the conservation status
- The difference in As content is large, therefore it is very likely that in some cases it was added deliberately to strengthen the resistance of the artefact

Materials characteristics effects on Powder Diffraction

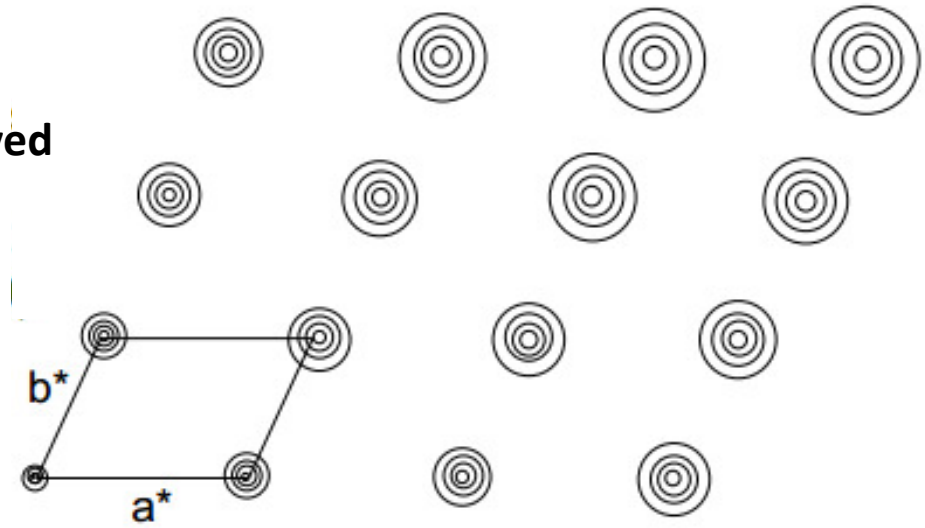
Peak broadening due to Grain Size and Residual Stress (Strain)

- **Peak shape analysis (average). The Diffraction peaks have a Lorentzian and a Gaussian component. The broadening of the witdh of the Lorentzian component with respect to a known standard (Si) can be related with residual strain. The broadening of the witdh of the Gaussian component with respect to a known standard (Si) can be related with grain size**

- **Direct measurement of lattice parameter (more precise and directional)**

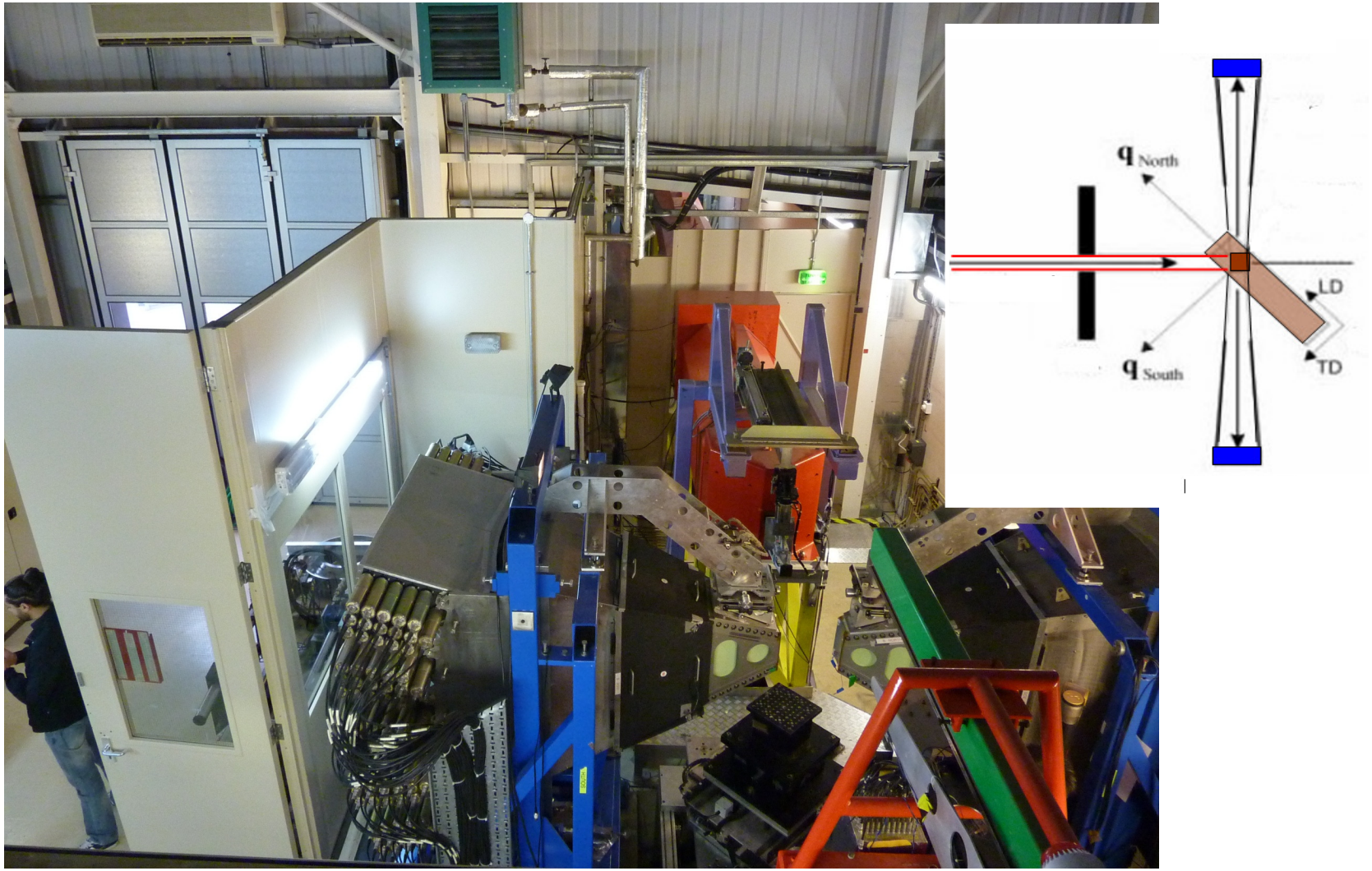
Residual stress

- Residual stress is what remain in a solid material after the original cause of the stress has been removed
- When a material has residual stressess present, some crystallite are compressed and some are streched, so the lattice parameter change
- It can be dependent of the direction

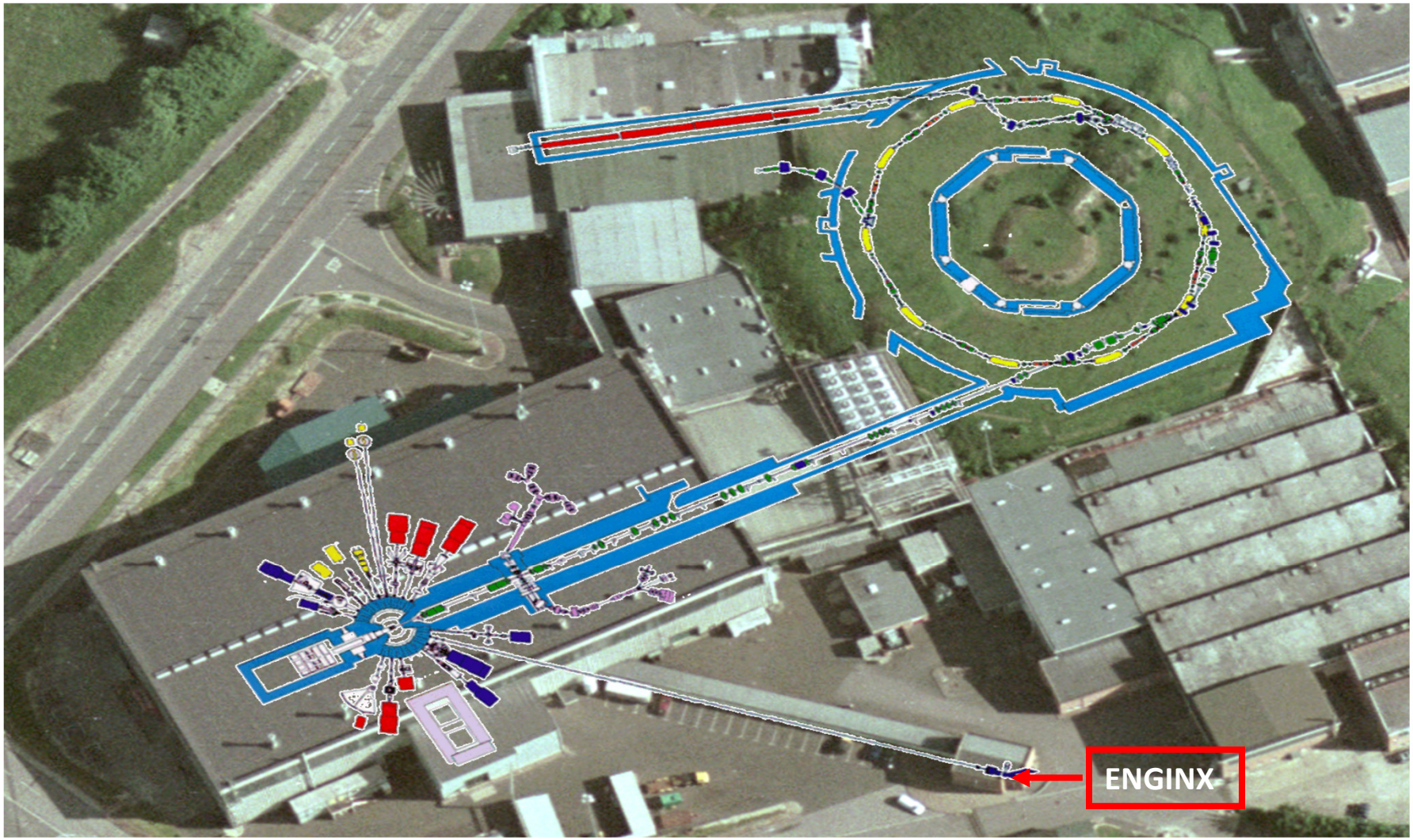


- Residual stress measurements are very important because can tell us something about the working techniques applied to our artefact
- Residual stress measurements are widely used to prevent premature failure of components or structures

ISIS strain scanner: ENGINX



The ISIS Spallation Neutron Source TS1



ISIS strain scanner: ENGINX

Primary flight path	50m
Secondary flight path 1.5m	1.5
Choppers	Disc choppers at 6.4m and 9.6m
Detectors	+/- 90° diffraction banks, ZnS scintillators, 3mm horizontal resolution. 10x10 pixel transmission detector (2.5mm square pixel pitch)
Detector Coverage	2q=76° to 104° Vertical coverage +/-21°
Wavelength Range	0.5-6Å
Incoming collimation - vertical	0.2 – 20 mm
Incoming collimation -horizontal	0.2 - 10 mm
Outgoing collimation - horizontal	0.5, 1, 2, 3 or 4 mm

Indian Shamshir

Single edge curved blade of 17th/18th century Hyderabad origin characterized at INES and ENGINX

Aim of the experiment

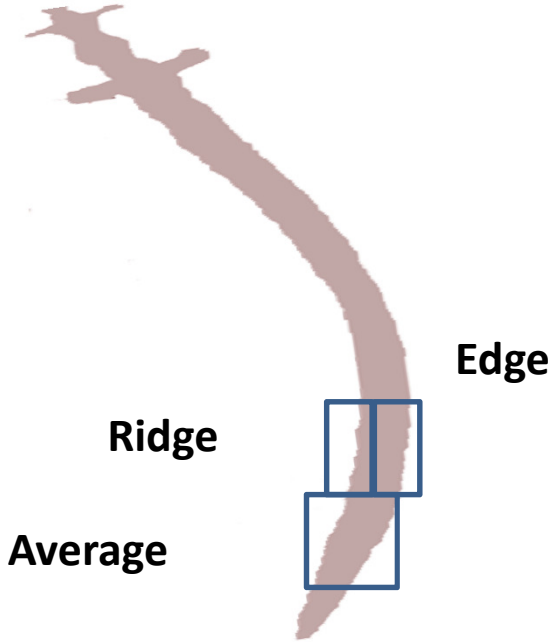
- Iron or Steel quality in different parts of the blade (iron phases, refinement, carbon content)
- Conservation status (presence of mineralization phases)
- Forging and assembly methods, technological manufacturing

Non invasive analysis

Shamshir @INES

Searched phases:

- ferrite, cementite, martensite: *metal phases*
- wuestite: *smelting*
- goethite, magnetite: *mineralization*
- hematite: *ore or mineralization*
- fayalite: *smelting*
- troilite: *carburization related*



Measured point	Ferrite	Cementite	Goethite	Hematite	Troilite
average	85.4(1)	13.6(2)	0.4(1)	0.4(1)	0.2(1)
edge	86.3(1)	12.9(2)	0.5(1)	0.3(1)	-
ridge	83.9(1)	13.2(2)	0.4(1)	0.4(1)	1.1(1)

Shamshir @INES

- **Ferrite: this is the room-temperature stable iron lattice based phase, which is the main component of iron and steel artefacts**

- **Cementite: this is the metastable intermetallic phase of iron carbide (Fe3C), its decay time is extremely long at room temperature (thousands of years) and is responsible for the hardness of steel.**

Amount of Carbon in the steel, found between 0.1% and 1% in the blade

Shamshir @INES

- **Wustite: this is the iron oxide phase (FeO). It is a result of incomplete reduction of the iron ore during the refining process. The amount of wustite within an alloy can be used as an index of the overall quality, of the smelting process**

- **Magnetite and hematite: these are also iron oxides (Fe_3O_4 and Fe_2O_3, respectively). These compounds are usually the starting material for ore reduction and represent, also, the final most stable results of the oxidation process. Their presence is thus an indication of the presence of raw ore or, alternatively, of some parts of the artefact being in a poor conservation condition**

Quality of the smelting process and poor conservation status. Our blade is very well conserved, refinement of the metal was very good

Shamshir @INES

- **Goethite: this is an iron oxide/hydroxide (FeOOH). This is a component of rust, being the first mineralization product formed on iron or steel objects. Its presence is usually an index of decay in the conservation status, and therefore gives information on the overall condition of an artefact**

Indication of poor conservation status.
Our blade is in very good conservation status

Shamshir @INES

- **Fayalite: this is an iron silicate (Fe2SiO4). It forms during smelting, by the reaction between iron oxides and the rocks where these are embedded, or a possible reaction with the walls of the furnace. Fayalite usually remains trapped inside the bloom, unless liquid iron or steel is formed during the smelting process, or unless the hot process is prolong enough to allow most of it to drip out of the bloom. Its amount is thus indicative of the length of the smelting process, as well as the temperature**

- **Troilite: this is an iron sulfide (FeS). It forms through diffusion of sulphur into the iron bloom during the smelting process. Sulphur is always present in the charcoal, which was commonly used in ancient furnaces and diffuses into the iron bloom in the same way as carbon does. Its value can be related directly to the amount of carbon in the bloom and to the type of charcoal used in the process**

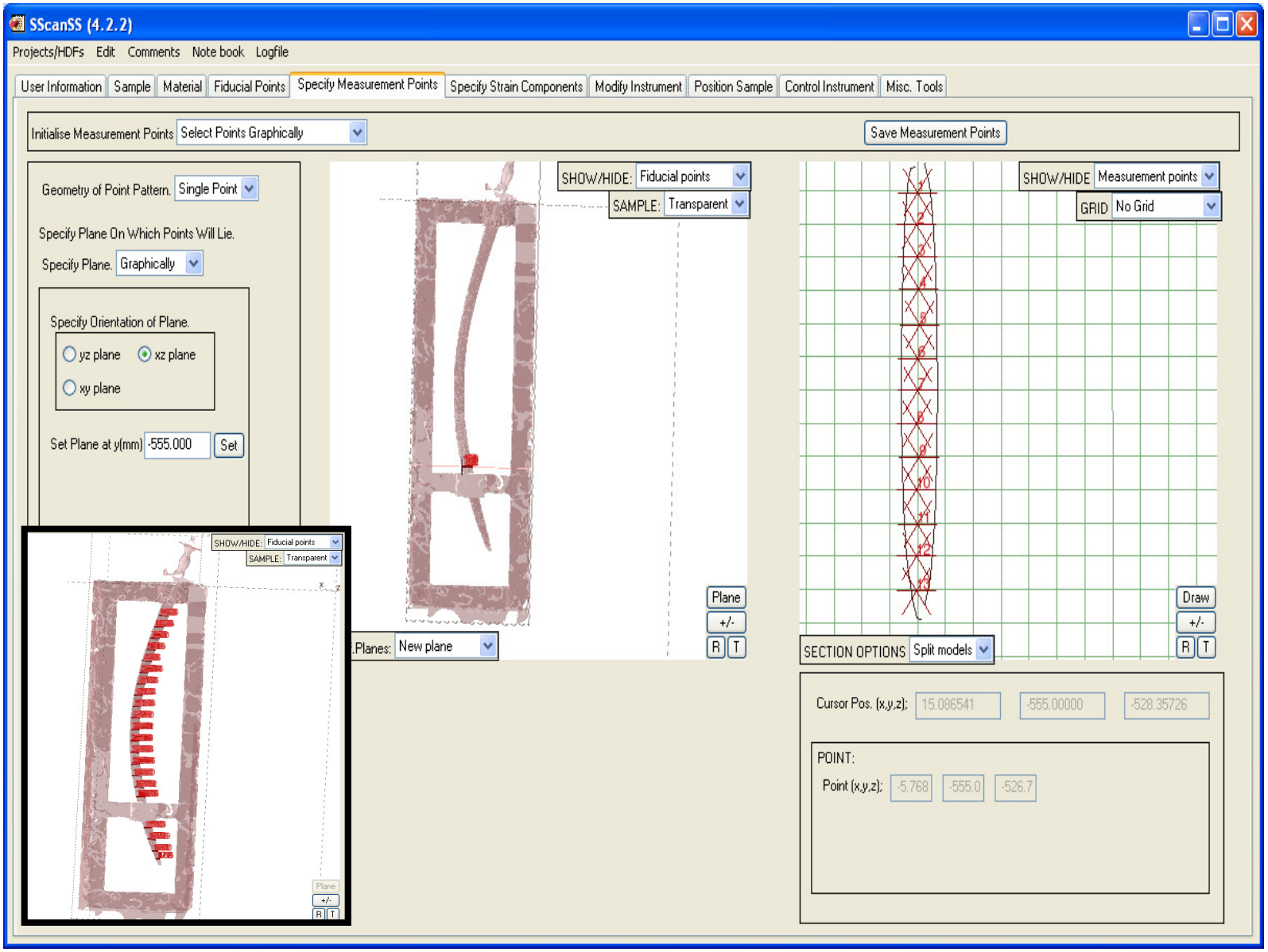
Shamshir @ENGINX

axial ↓

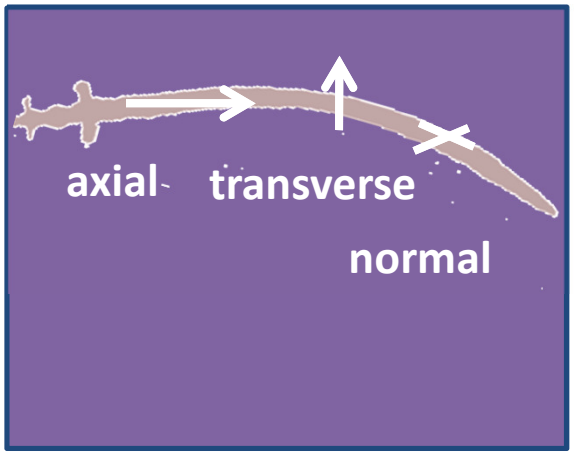
transverse →

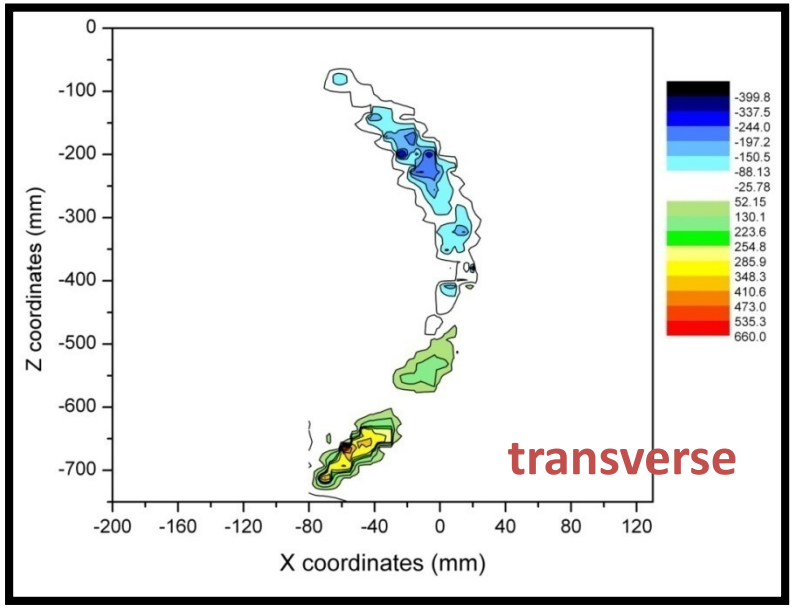
normal ×

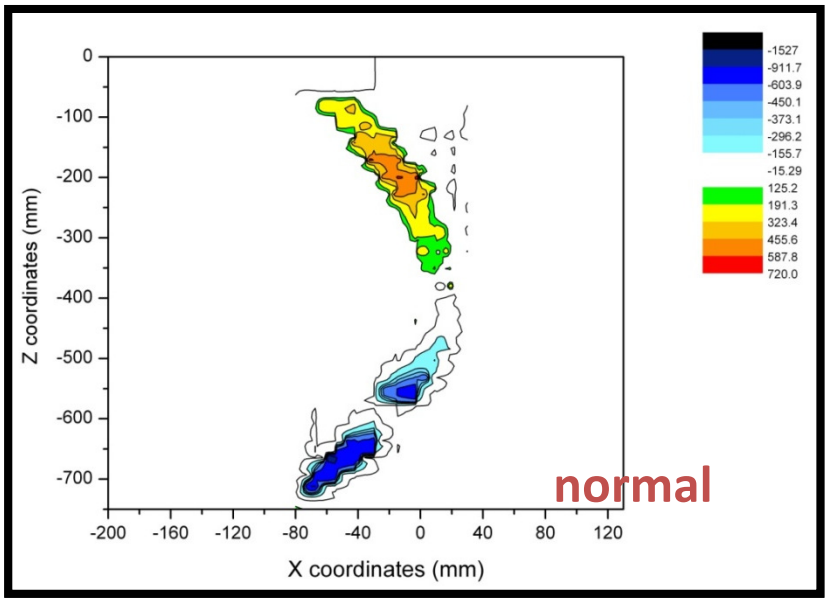
Shamshir @ENGINX

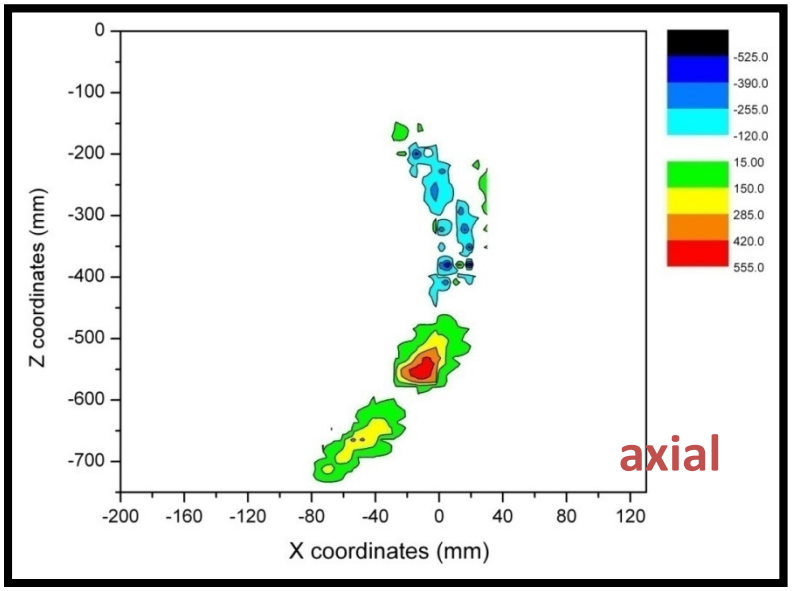


Strain measurements









Shamshir @ENGINX conclusions

- **Information about the composition of the samples have been non destructively obtained through ToF-ND. High quality well preserved steel: very low non metallic phases (mineralization, slags) (INES)**

- **The forging method is substantially different in the upper and lower part: presenting an opposite strain distribution (ENGIN-X)**

- **The combination of two different instruments for diffraction, whit different characteristics, represents the ideal complement for archaeometallurgical samples characterization**

Materials characteristics effects on Powder Diffraction

Texture (change in peaks intensity due to preferred orientation)

- **Rietveld refinement (J index)**
- **Direct texture measurements**

Texture

Analysis of the statistical distribution of the crystallographic orientations in a polycristalline material, gives hints about working techniques (casting, hammering, quenching…)

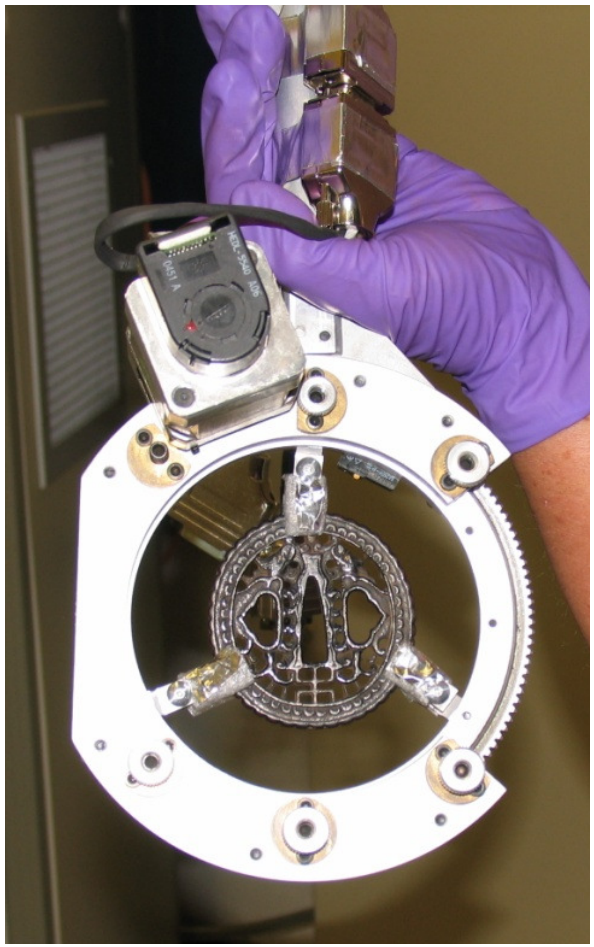
Bragg peak intensity variation as a function of the sample orientation can be corrected using Orientation Distribution Function (ODF)

$$J = 1 + \sum_{L=2}^{N_L} \frac{1}{2L+1} \sum_{m=-L}^{L} \sum_{n=-L}^{L} |C_L^{mn}|^2$$

J=1 No texture
J=∞ single crystal
J>1 textured sample

C coefficient are related with the sphrical harmonics terms used in the ODF to account for anysotropy, to better fit our data

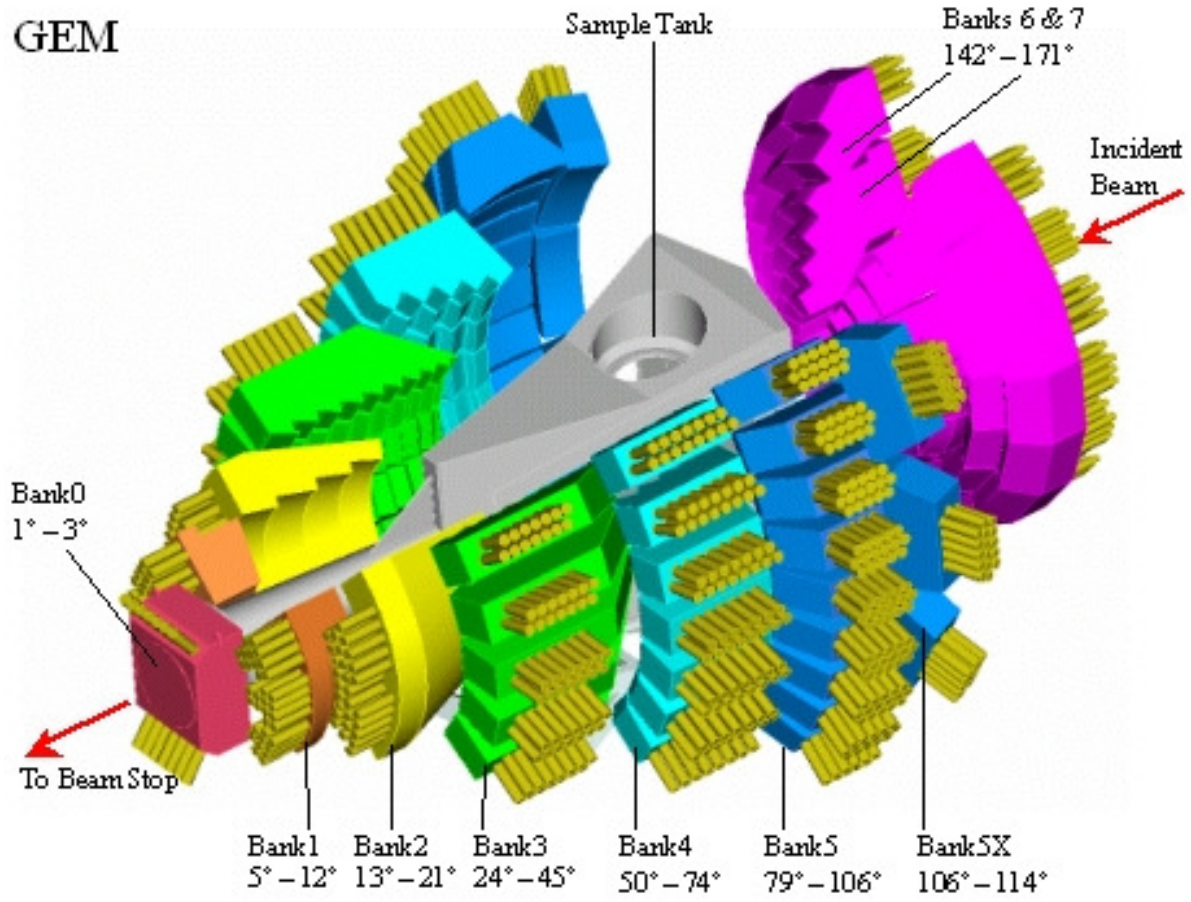
Texture



- To evaluate the anisotropy of the grain orientation distribution in the sample we have to put the sample in a goniometer, then collect diffraction spectra at several angle (ideally every 10^0). VERY LONG MEASUREMENTS

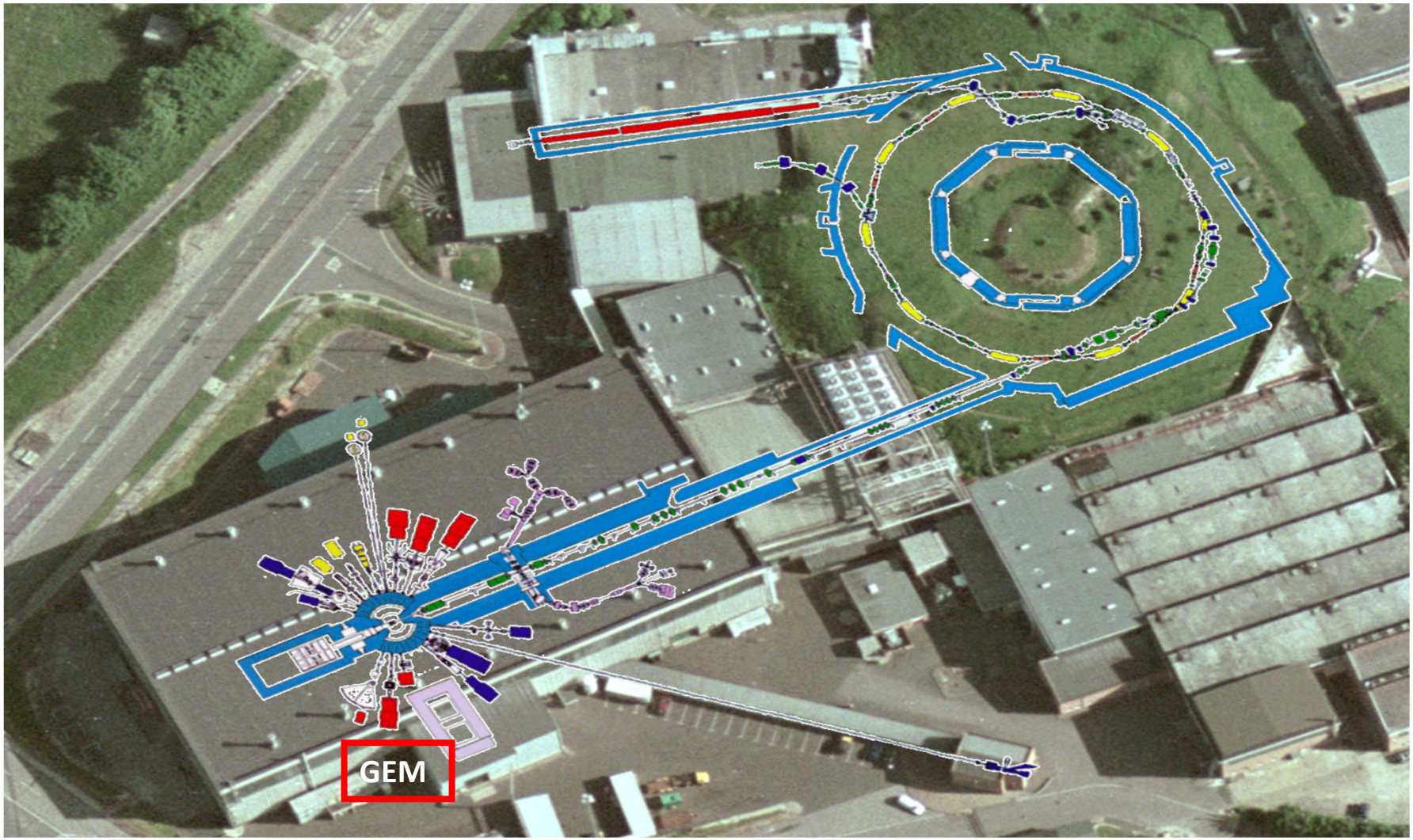
- We use MAUD not GSAS

GEM @ISIS



Large angular coverage!!!

The ISIS Spallation Neutron Source TS1



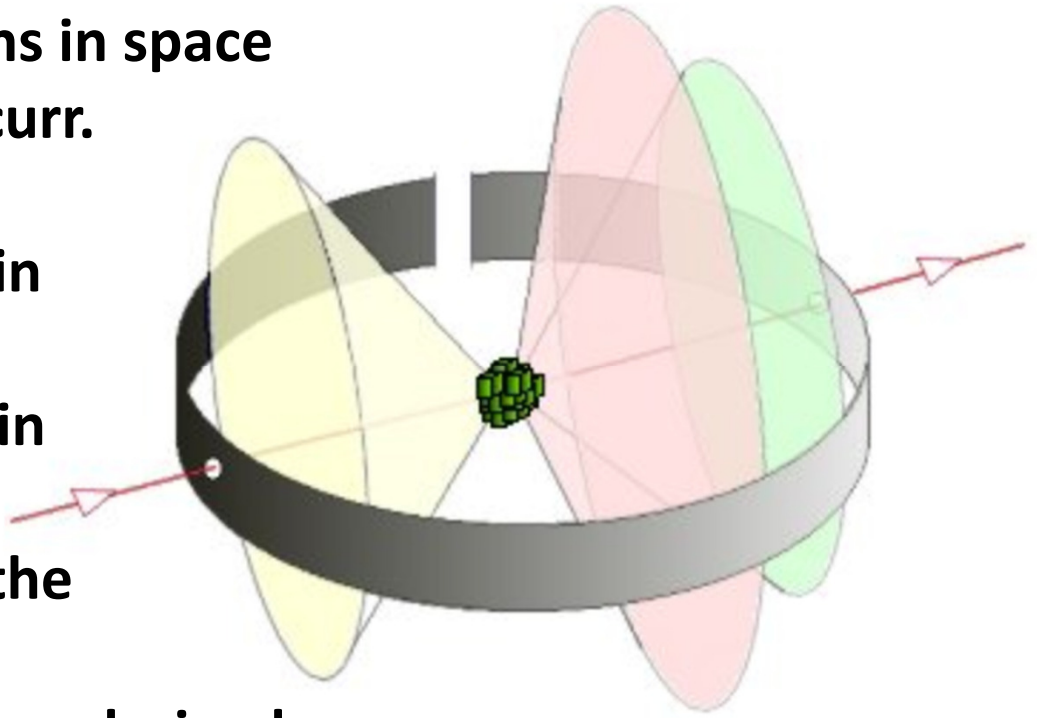
GEM @ISIS

Key Facts

- ❑ **The GEM detector array was completed in December 2003**
- ❑ **The completed GEM detector array has 7270 elements (not including monitors) in 86 modules**
- ❑ **The GEM shutter was opened for the first time on 12th October 1999**
- ❑ **The GEM detectors cover a scattering angle range from 1.1° to 169.3°**
- ❑ **GEM's incident flight path is L1=17.0 metres**
- ❑ **GEM's scattered flight path ranges from 1.0 metres to 2.9 metres**
- ❑ **The GEM vacuum vessel has a volume of 1.3517m3 (i.e. 1351.7 litres)**

GEM @ISIS

- GEM detector coverage match very well the Debye Sherrer cone shape of the positions in space where diffraction occurr.
- We can measure the anisotropy in the grain distribution by refining the change in intensity of the diffraction peaks on the Debye Sherrer cones
- Texture information are derived from only one measurement (no need for rotation



GEM versus INES

Why do we use INES and not GEM all the time?

- **Backscattering resolution is higher on INES (better for alloy characterization)**
- **GEM tank is different compared to INES, therefore not all the sample that can go on INES can go on GEM. GEM tank is not easily accessible**
- **No NRCA on GEM**
- **No alignment devices, no possibility to do scan on the sample**

Thank you for your attention!