The Italian Neutron Experimental Station (INES) at ISIS

State of the Art and applications

Francesco Grazzi

Consiglio Nazionale delle Ricerche

Istituto dei Sistemi Complessi, Sezione di Firenze

Consiglio Nazionale delle Ricerche

Summary

INES timeline and people
Neutron characteristics
Time of flight diffraction
INES characteristics
INES features
- software available
- special devices

INES applications
- metal characterization
- archaeometry

A case study

INES timeline & people

2004: Project and components building

2005: Installation and calibration

2006: commissioning and first users

2007-2009: standard user program

Marco Zoppi: instrument responsible

Francesco Grazzi: development and tests

Antonella Scherillo: instrument scientist

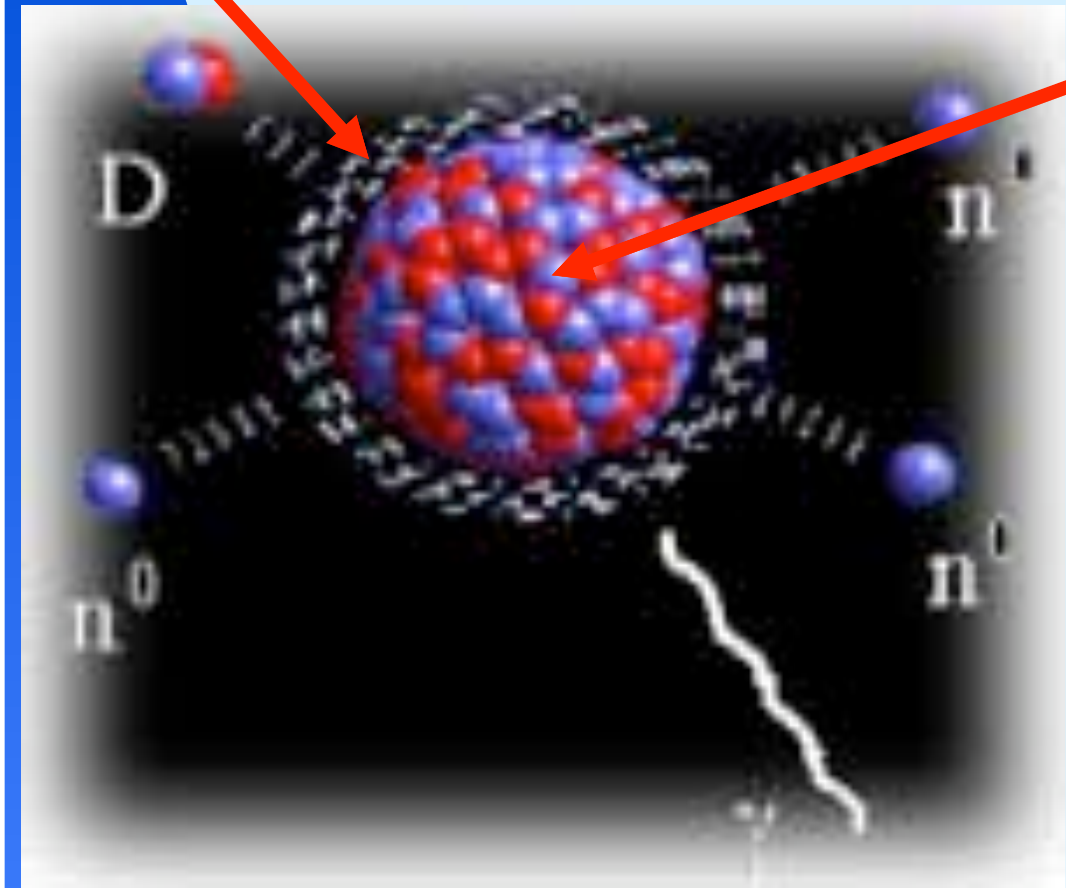
Silvia Imberti, Laura Bartoli: prev. instr. scient.

Consiglio Nazionale delle Ricerche

How are neutrons produced?

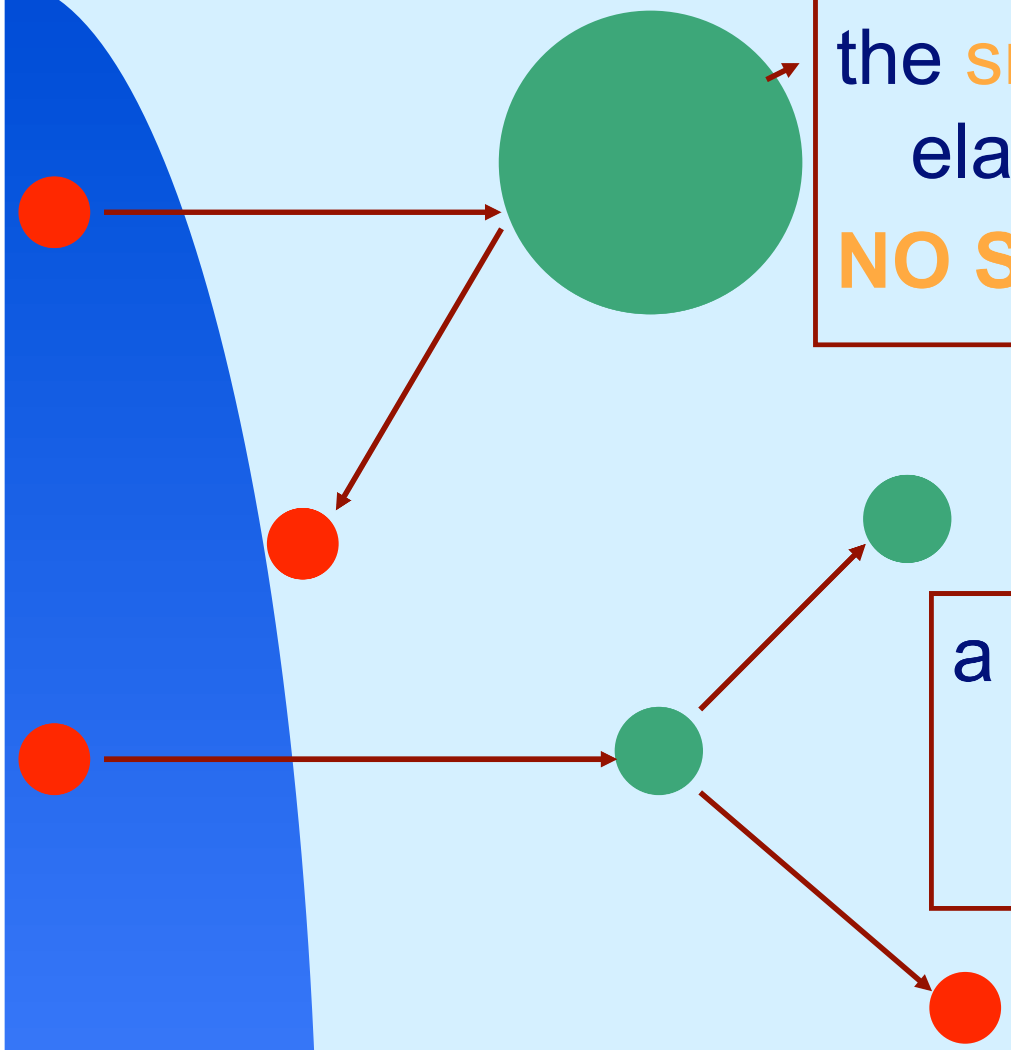
High energy protons

Target: Tungsten



- Protons disrupt the target atoms
- Broken in pieces:
  - producing light nuclides and neutrons
- 15-30 neutrons / event
  - very energetic neutrons

Fast neutrons are "moderated"



the small mass **m** bouches elastically on a large mass **M**

NO SPEED LOSS!!

a small mass **m** transfers momentum when hitting a similar mass **m'**

speed loss ⟹ moderation

thermal neutrons

i.e. moderated using H-rich materials at room temperature

- energy: $E \cong kT$ ($\cong$ 25 meV)
- wavelength: $\lambda \cong 0.18$ nm
- thermal neutrons are a “gentle” probe for dense matter

ADVANTAGES:

- neutrons have the correct wavelength
- neutrons have a high penetration power

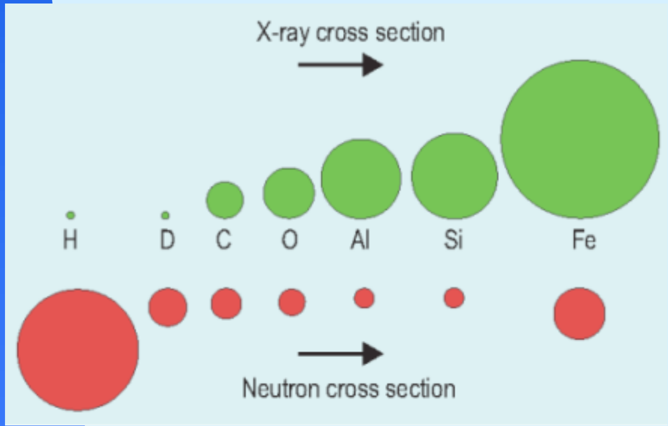
DISADVANTAGE

- neutron experiments are EXPENSIVE

Consiglio Nazionale delle Ricerche

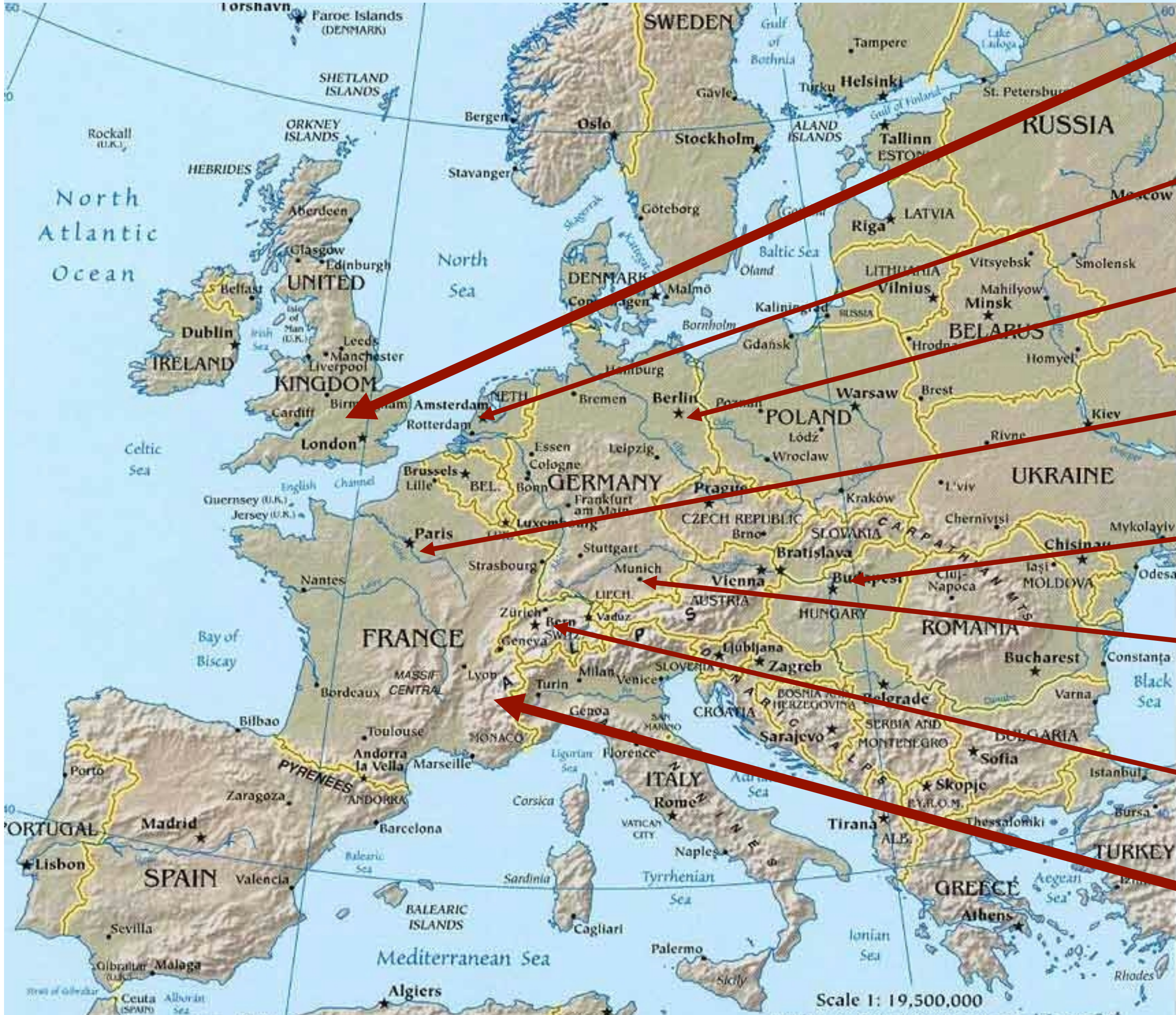
Neutrons versus X-rays
(non-invasive, non-destructive techniques)

X-rays	neutrons
Electron-interaction	Nuclear-interaction
Surface limited	Bulk analysis
Punctual properties	Average properties



Especially on METALS
Neutrons provide
Quantitative multiphase bulk
compositions

where neutrons?

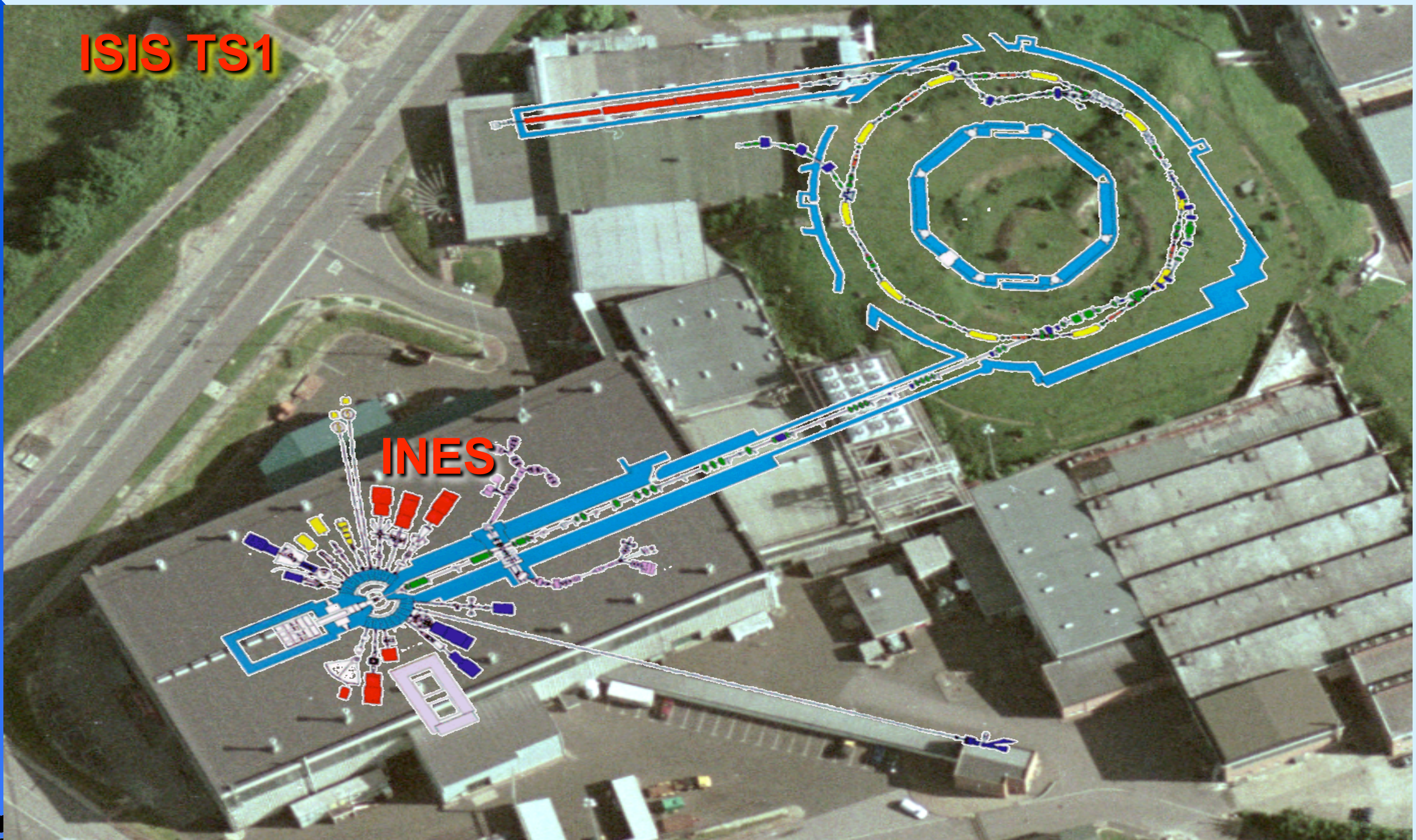


- ISIS (U.K.)
- IRI (NL)
- HMI (De)
- LLB (F)
- KFKI (H)
- FRM II (De)
- PSI (CH)
- ILL (F)

Consiglio Nazionale delle Ricerche

STFC campus (UK)

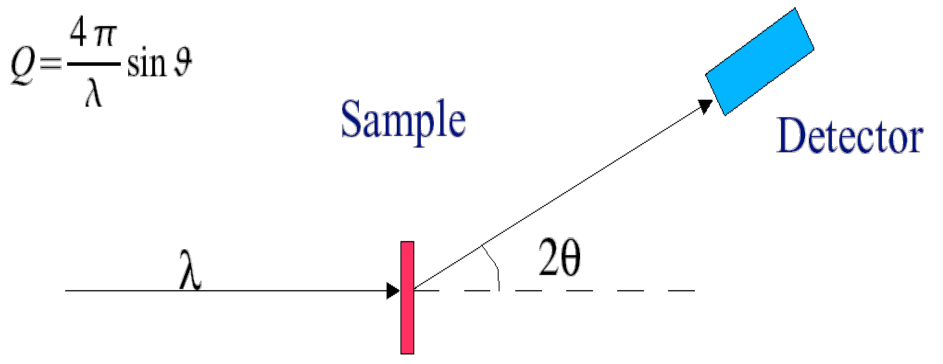
The CNR instrument: INES@ISIS



Properties of thermal neutrons

No electric charge

High penetration power into dense materials



- **λ = 1.78 Å = 0.178 nm**

  ~ inter-atomic distances in solids

$$d_{hkl} = \frac{h}{m_n} \cdot \frac{1}{L} \cdot \frac{t_{hkl}}{2 \cdot \sin(\Theta)}$$

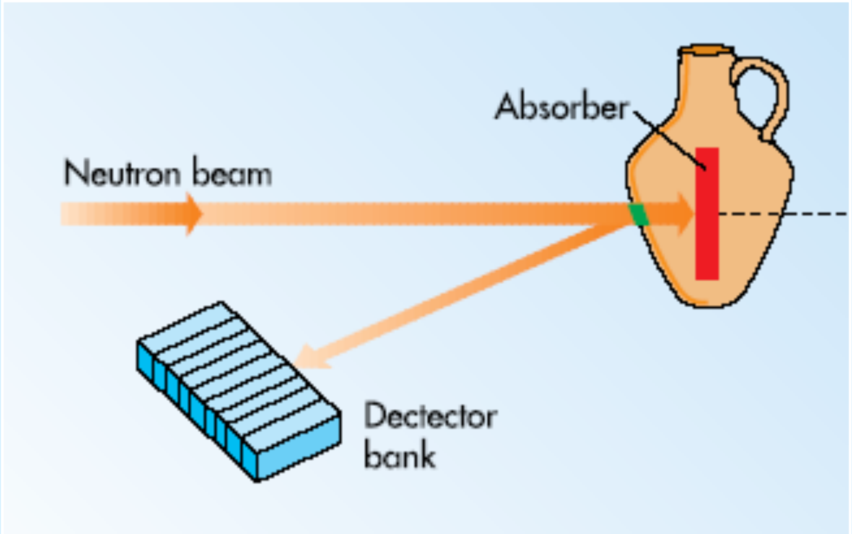
- **Bragg diffraction of dense metals**

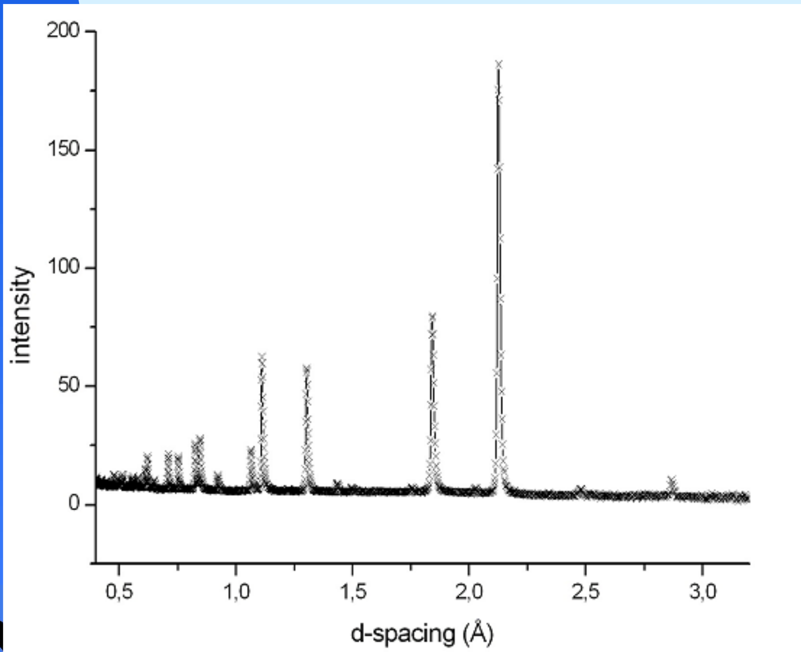
ToF neutron diffraction

Non destructive, non invasive characterization technique

Sample characterization in terms of:

- crystal phase(s)
- texture
- residual stress

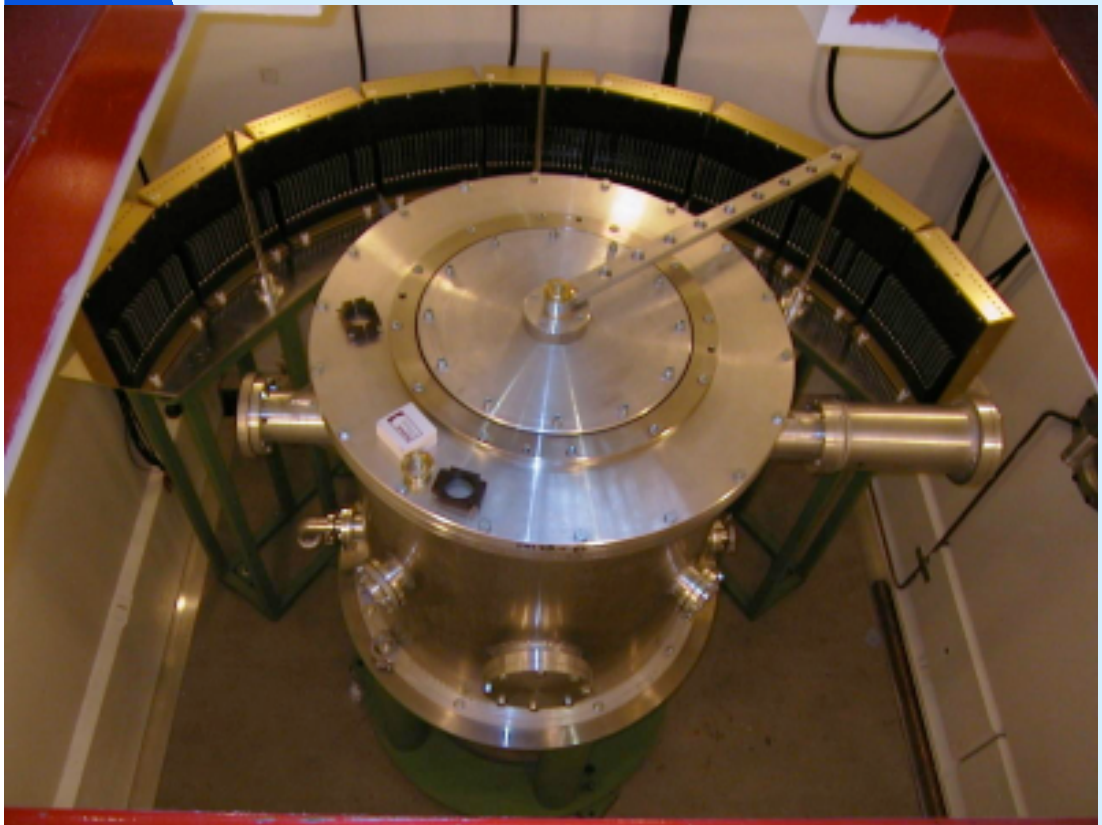




Measured Diffraction Pattern

Consiglio Nazionale delle Ricerche

The Italian Neutron Experimental Station (INES@ISIS)



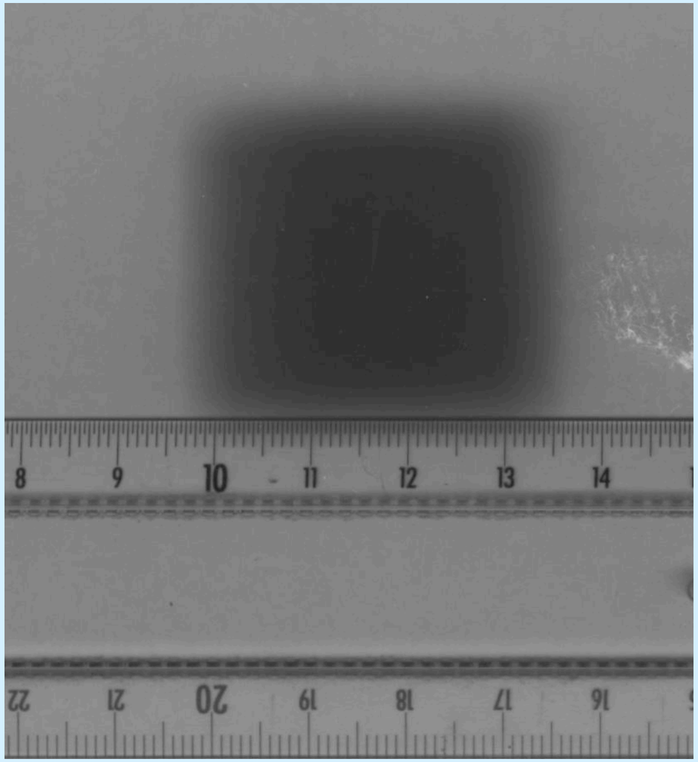
INES diffractometer features

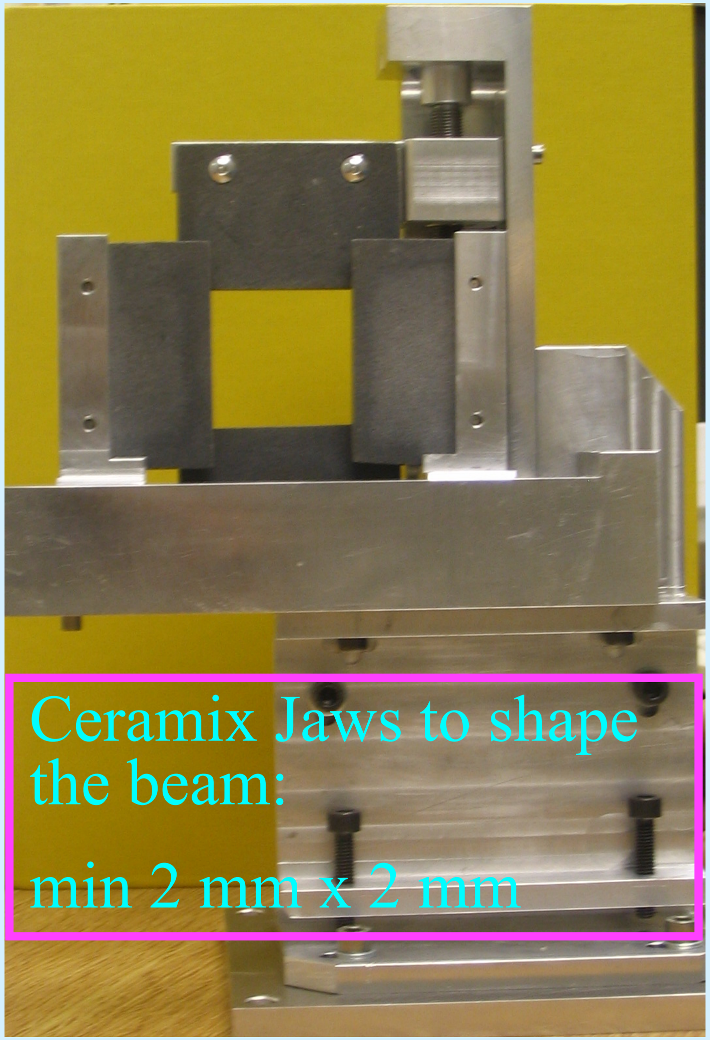
- water moderator
- primary flight path 22.804 m
- secondary flight path 1.000 m
- 9 banks (144 ^{3}He squashed detectors)
- λ range: 0.17 – 3.24 Å
- 2θ range: 11.6°-170.6°
- d range: 0.1-16 Å
- Resolution: 0.1% - 1%

Consiglio Nazionale delle Ricerche

INES beam characteristics

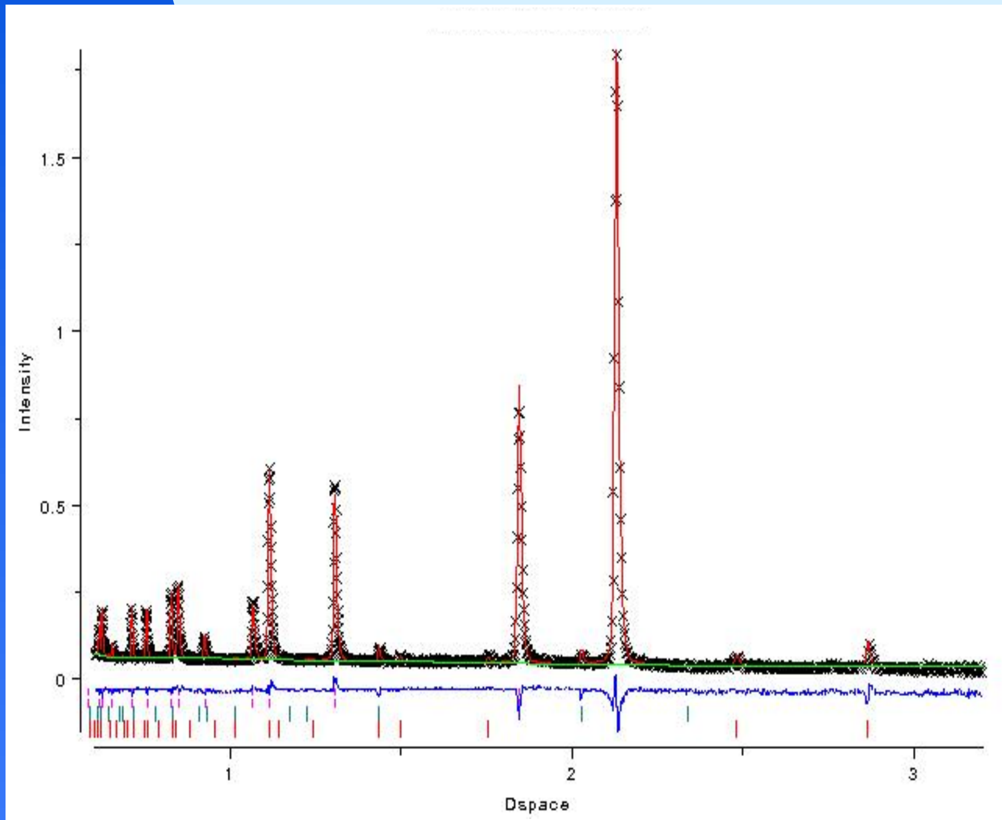
- Small penumbra
- Regular square shape of the beam
- Beam size 38 mm x 38 mm





How to perform a measurement

Collecting data for several hours...



...analyse the diffraction pattern

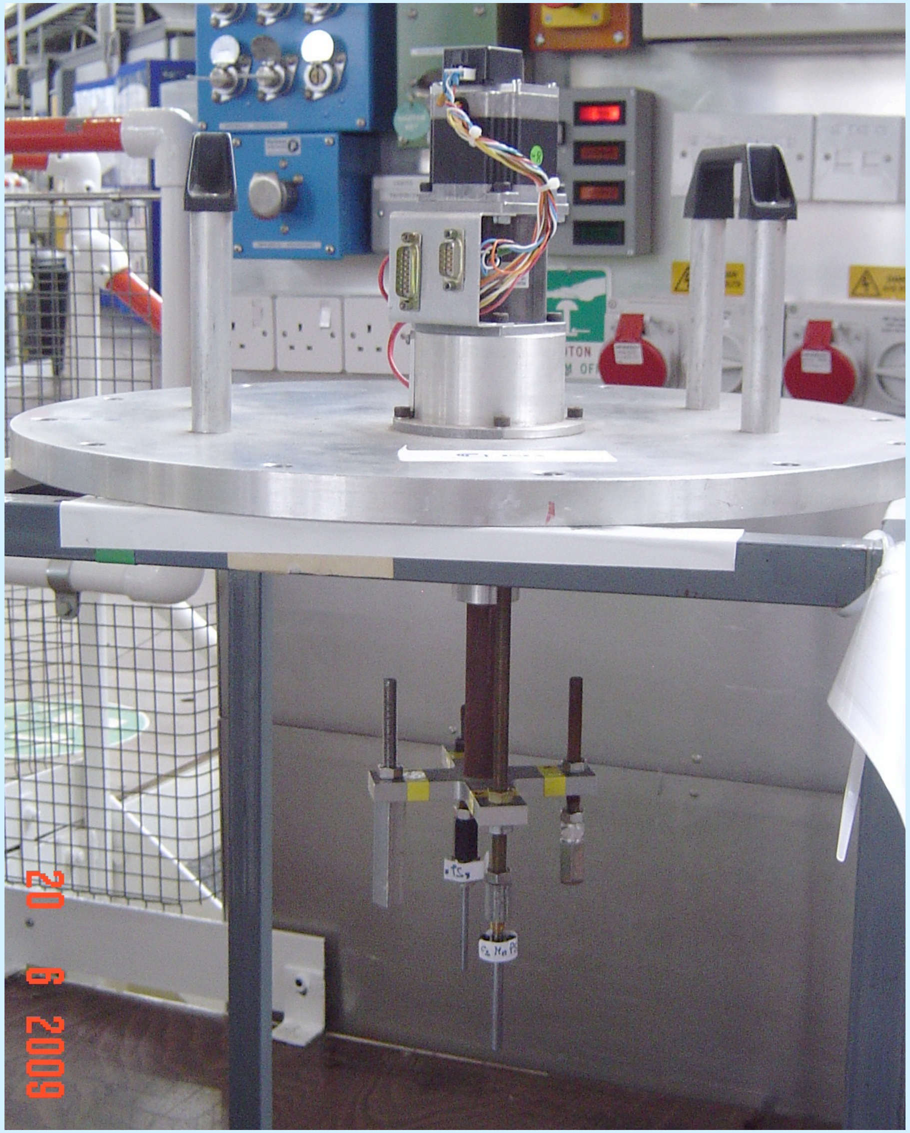
Ternary Alloy:	
Cu:	88 wt %
Sn:	9.4 wt %
Pb:	2.6 wt %

Consiglio Nazionale delle Ricerche

INES special devices

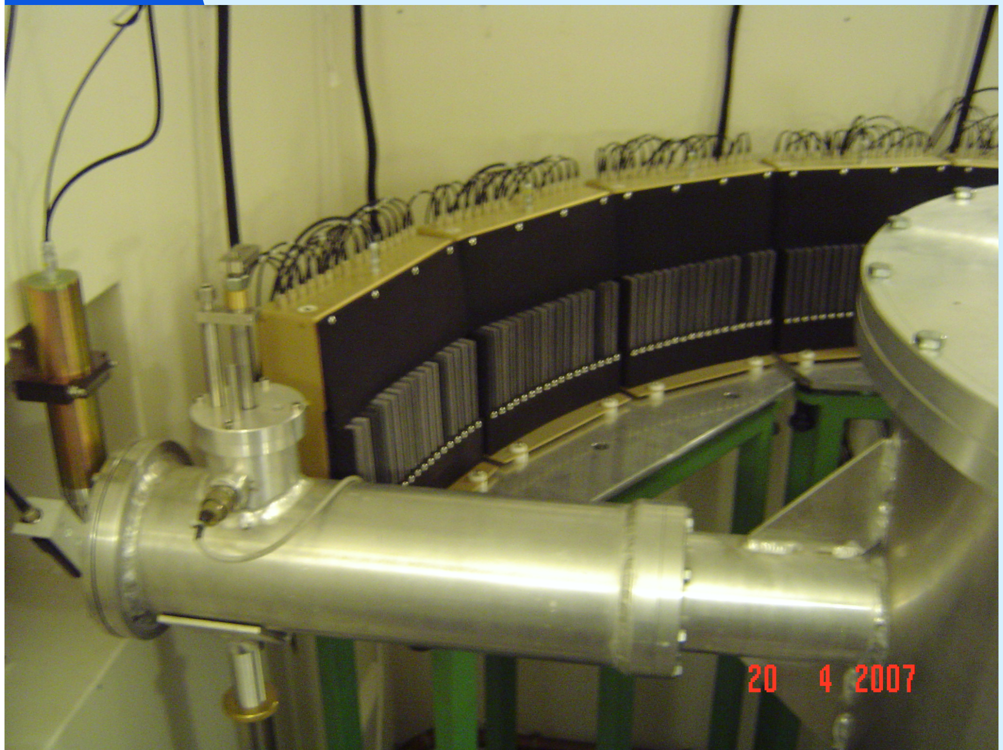
4 positions

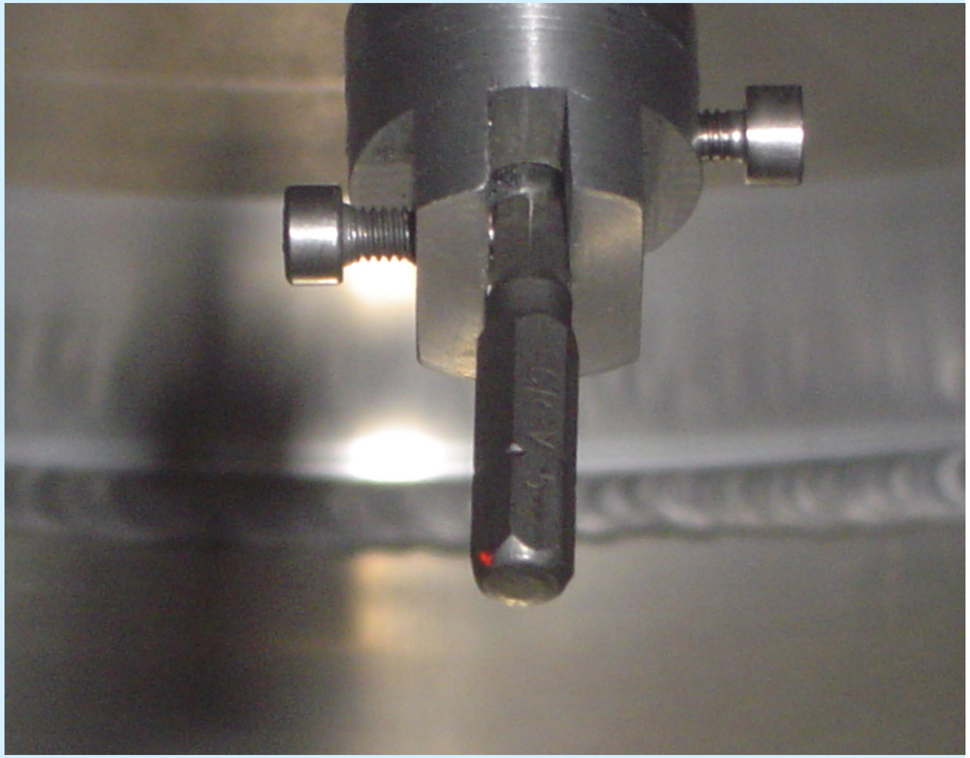
sample changer



INES special devices

Laser pointer collinear with neutrons
to know where to place the sample

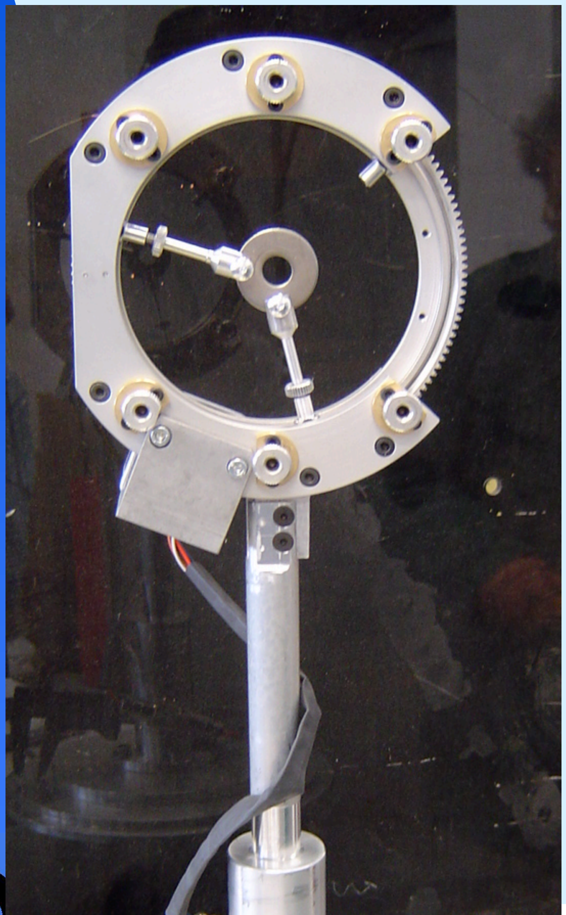




Consiglio Nazionale delle Ricerche

INES special devices

Single axis goniometer to change the sample orientation with respect to beam and detectors

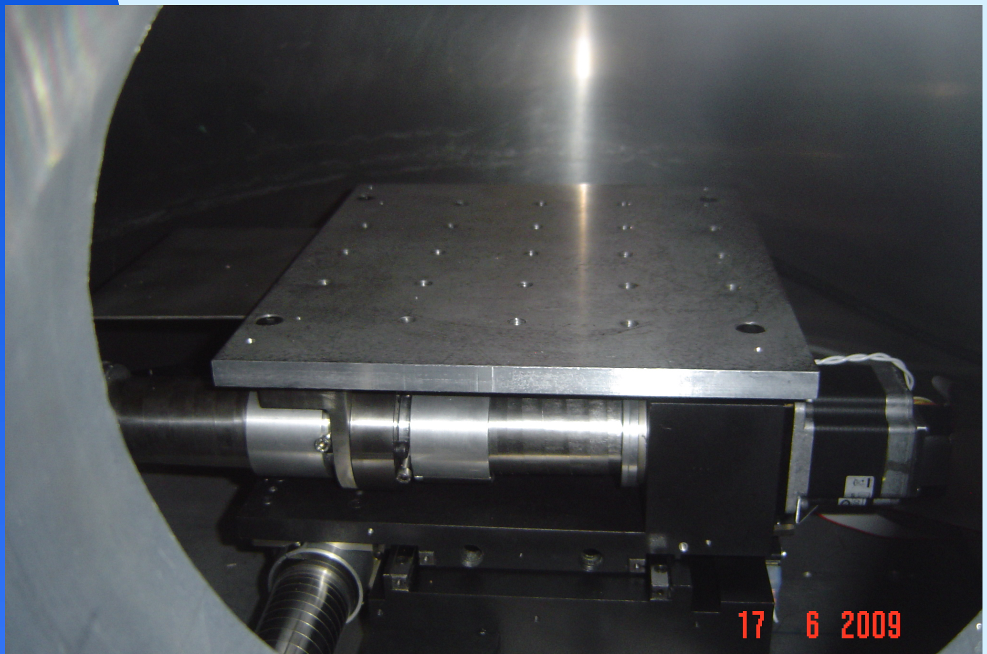


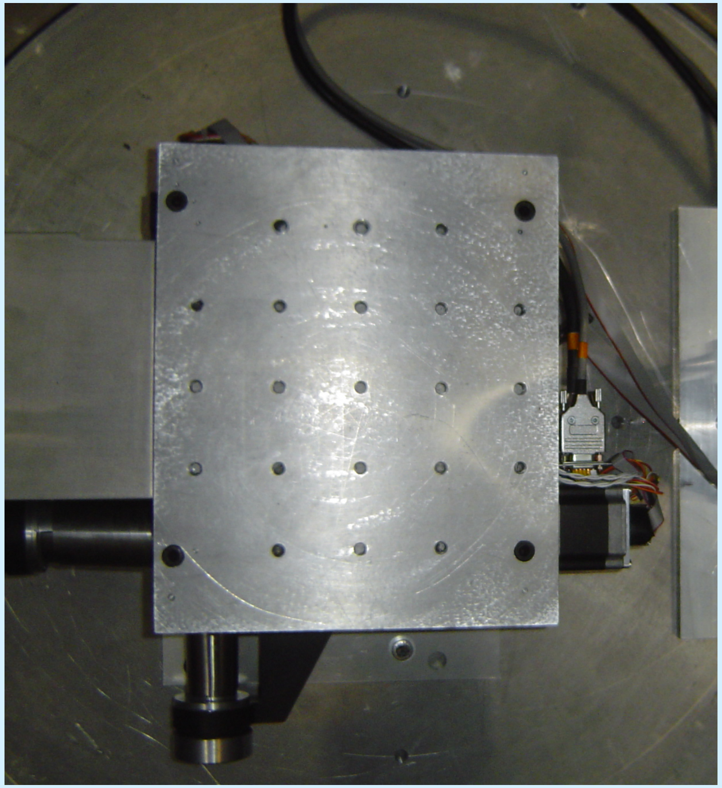
- 120 mm sample diameter
- Max weight allowable 1 kg.
- Stepping motor, 0.2° min. step
- Backlash avoid system
- External programmed and dynamic electric input
- Fast and easy insertion and removal (1 operator, no crane)

Consiglio Nazionale delle Ricerche

INES special devices

X-Y table to move large scale samples



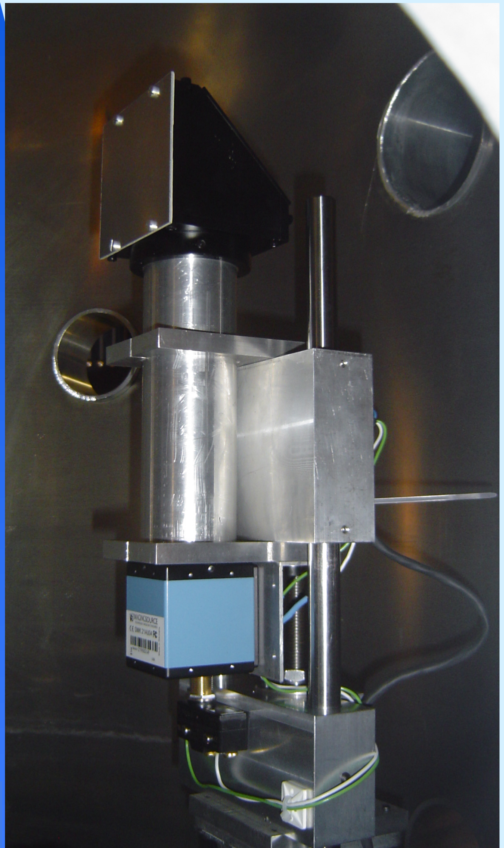


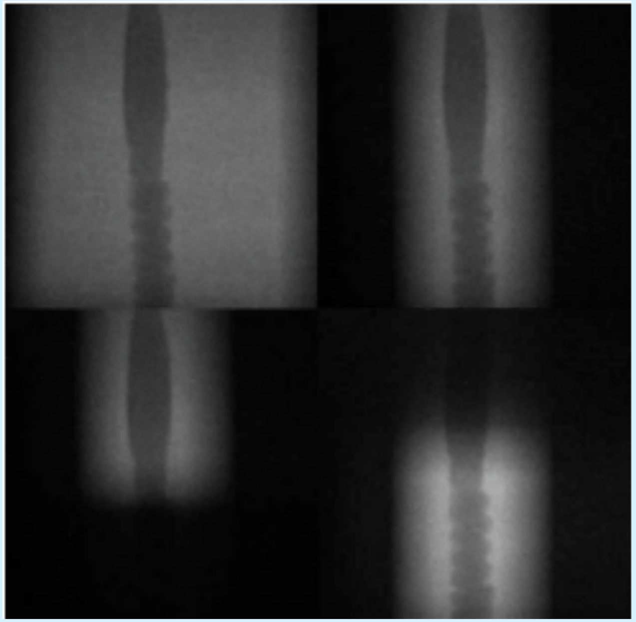
Consiglio Nazionale delle Ricerche

INES special devices

Removable beam aligner to select gauge volumes

to be analysed in the sample

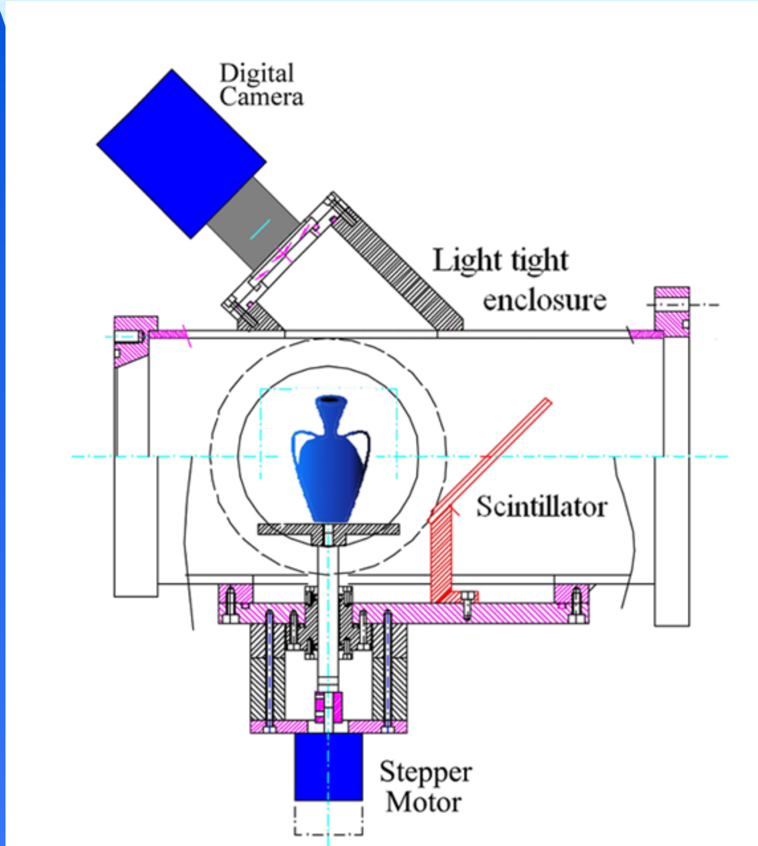


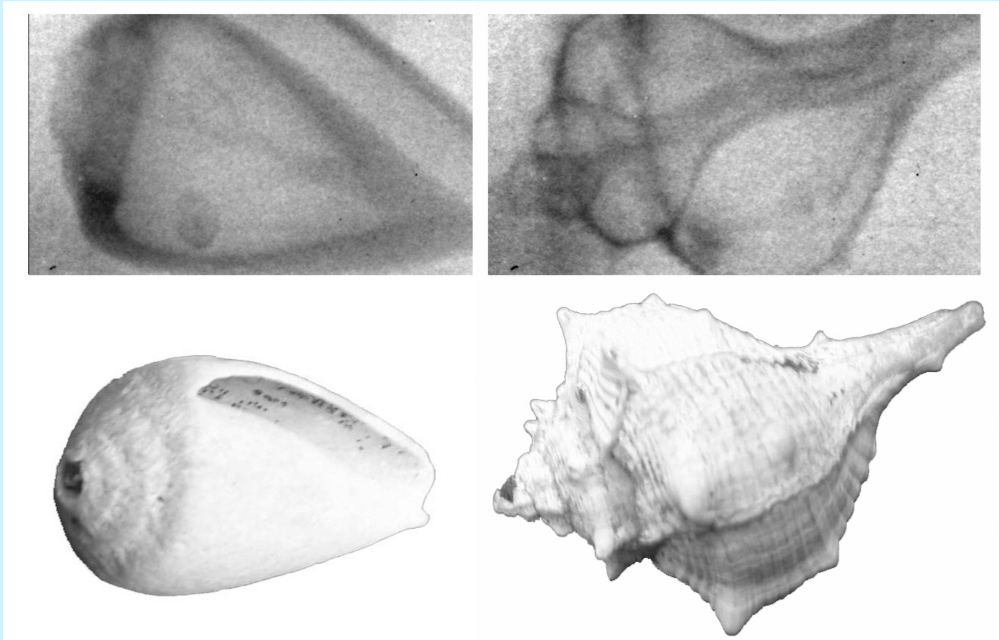


Consiglio Nazionale delle Ricerche

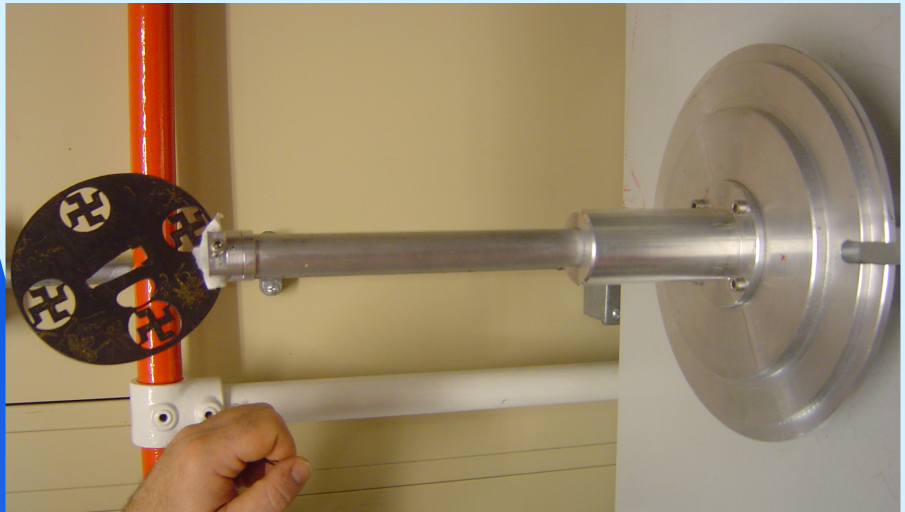
INES special devices

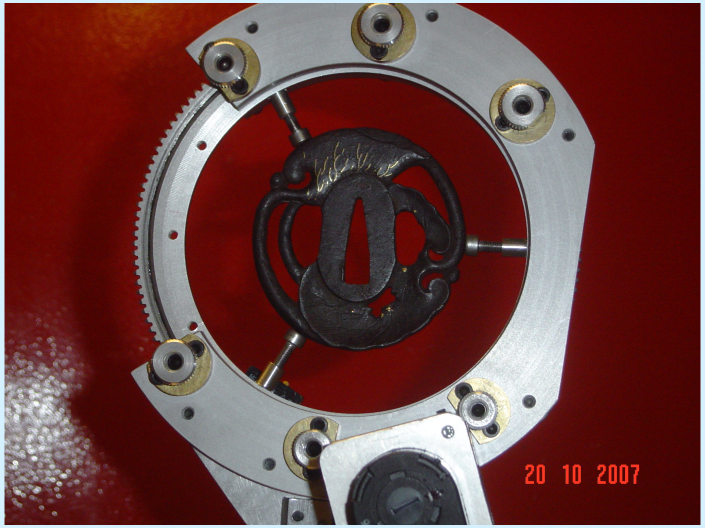
Imaging and tomographic device





Neutron diffraction measurement on INES



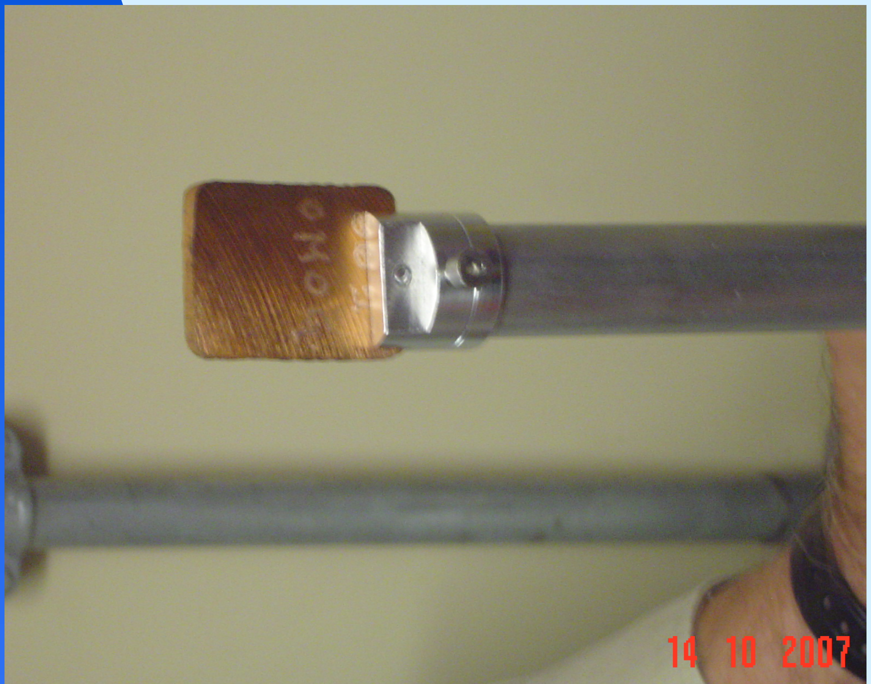


Quantitative multiphase and peak shape analysis (1-8 hours)

Texture orientation and analysis (12-24 hours)

Consiglio Nazionale delle Ricerche

Measurements on standard



Copper and copper alloys:

Calibration curves for annealed

Cu-As (0-7% wt. As)

Cu-Sn (0-14% wt. Sn)

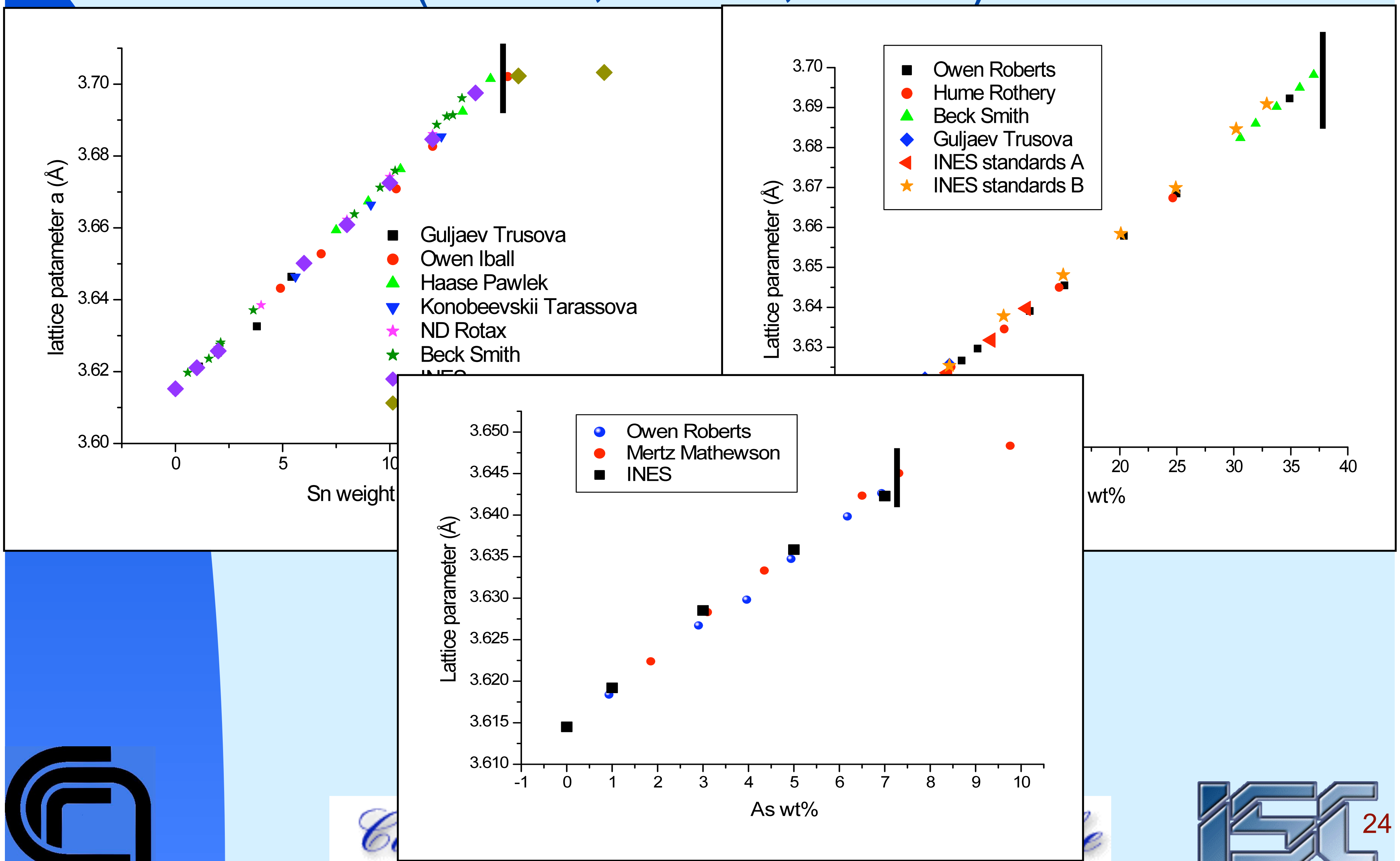
Cu-Zn (0-33% wt. Zn)

Cu-Sb (0-11% wt. Sb)

Cu-Ni (0-100% wt. Ni)

The most common copper alloys of the ancient and historical times

Calibration curves
(Cu-Sn, Cu-Zn, Cu-As)



Importance of a good calibration

Quaternary alloy (Ghiberti):

Pb 1.32±0.06

Cu 82.8±0.2

Sn 3.07±0.09

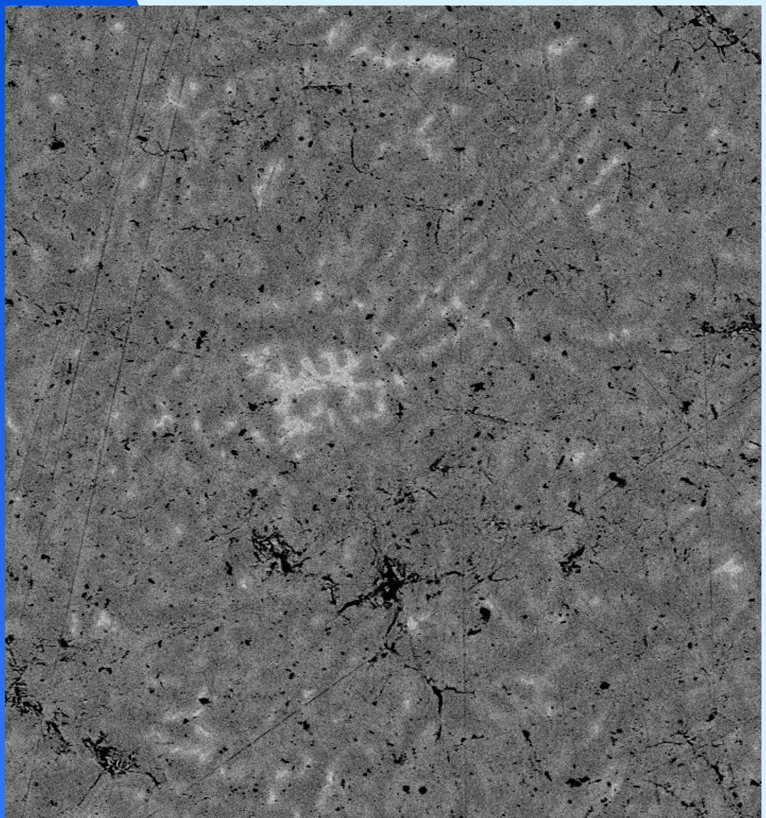
Zn 12.8±0.2

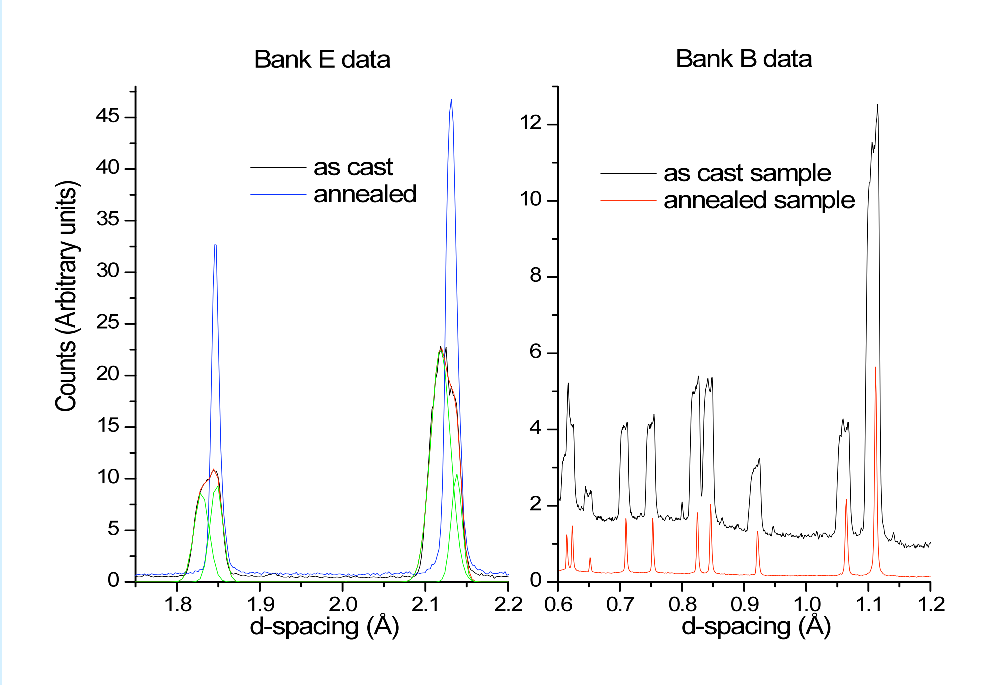
Calculated (cal. curves): a=3.663±0.003

Measured: a=3.662±0.002

Observation
of two different compositions in as-cast samples

ESEM picture





INES diffraction pattern

2 lattice parameters:

a_1=3.6619 (62% weight)

a_2=3.6861 (38% weight)

Consiglio Nazionale delle Ricerche

Quantitative analysis of historical samples

Bronze celtic spiral fibula

50.0% bronze (a=3.667Å)

(inner Sn wt 8.9%)

6.5% lead

28.2% cuprite (Cu_2O)

3.4% tenorite (CuO)

8.2% nantokite (CuCl)

3.7% paratacamite (CuCl+H_2O)

This sample has copper illness!!

Consiglio Nazionale delle Ricerche

A research application in archaeometry

Research project for non invasive

characterization of Japanese artworks

Cooperation agreement between

Stibbert Museum

CNR-ISC

Characterization of steel and copper alloys metal artefacts

Characterization of Japanese pigments

Instrumentation and techniques

Time of Flight Neutron Diffraction: quantitative non invasive characterization of phase components, determination of working techniques (INES@ISIS)

SEM-EDX analysis: done on whole samples, non invasive characterization of surface treatments and composition of the metal alloys.

Vickers Micro-Hardness Measurements:
Micro invasive characterization of carburization and thermal treatments of Japanese steel blades.

Raman, FORS, SEM-EDX: identification of Japanese pigments in ancient paper and silk paintings

Experiments performed

a) Characterization of four tsubas of a private collection through combined use of Time of Flight Neutron Diffraction and SEM-EDX

b) Quantitative characterization of seven blade fragments from a private collection through Neutron Diffraction, phase analysis and carbon content

c) Vickers Micro-Hardness Measurements of 100 Stibbert Museum blades on edge core and ridge and database built up

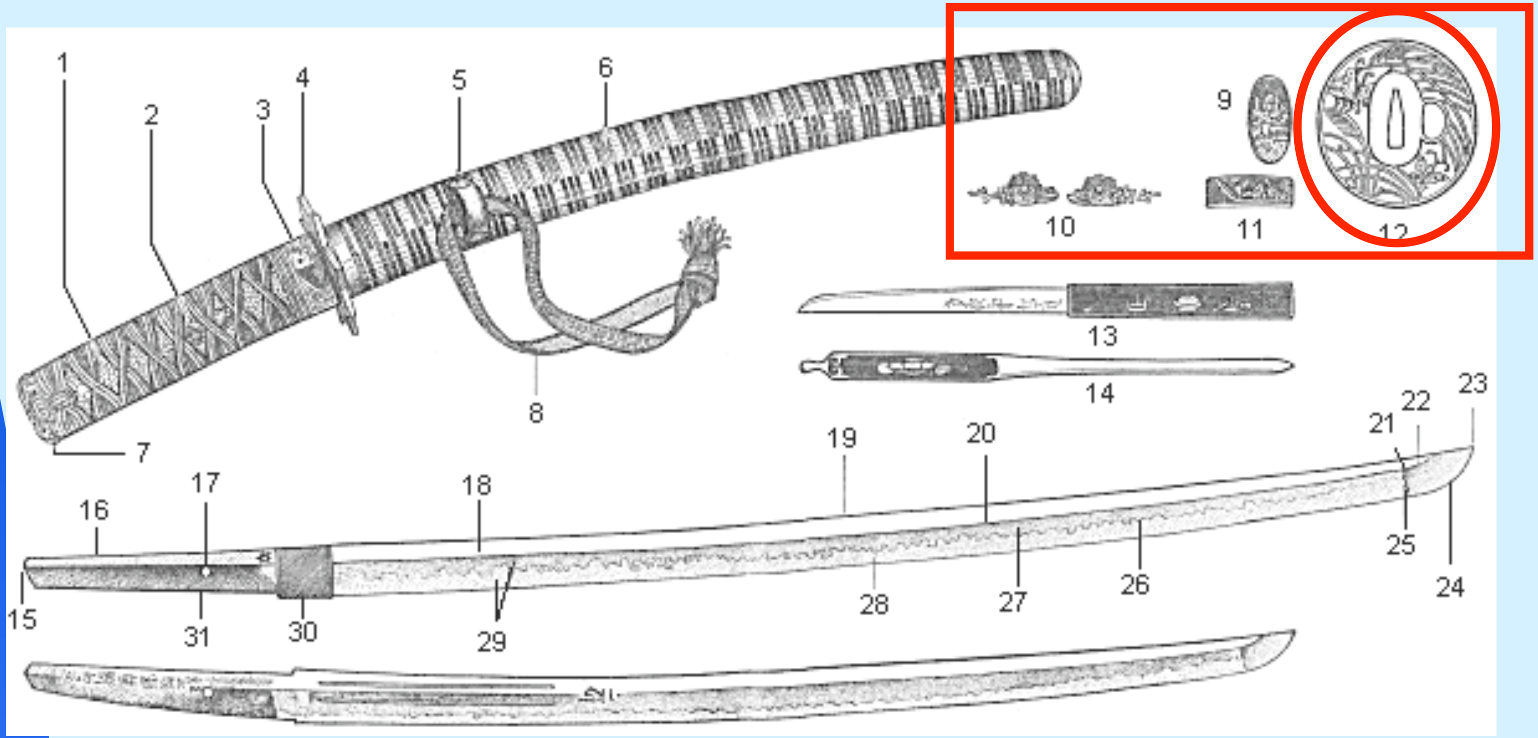
d) Characterization of 11 Stibbert Museum tsubas through Time of Flight Neutron Diffraction

e) Quantitative characterization of two whole long blades through neutron diffraction: phase analysis, carbon content and stress and strain map.

f) Build up of a Raman spectra database of 32 Japanese pigments and application to a 18th Century paper painting.

Experiment a)

Japanese sword characterization



Sword hand guard (Tsuba)

Experiment a)

Scientific analysis

- •Phase composition of the core
- •Working techniques

} Neutron diffraction

- •Garnish application and composition
- •Patination

} SEM EDX

SEM-EDX: detailed surface analysis of the whole sample (ESEM Quanta-200 FEI)

Neutron diffraction: quantitative bulk characterization of the whole sample through Rietveld Refinment - GSAS code (INES@ISIS)

Experiment a)

Diffraction

Quantitative multiphase analysis

Sample	Phase (wt%)					
	ferrite	cementite	martensite		C (wt%)	
T1	97.4	2.1	0.5	>	0.2	(steel)
T2	100.0	0.0	0.0	>	0	(pure iron)
T3	98.8	1.2	0.0	>	0.1	(wrought iron)

	copper alpha phase
T4	100.0%

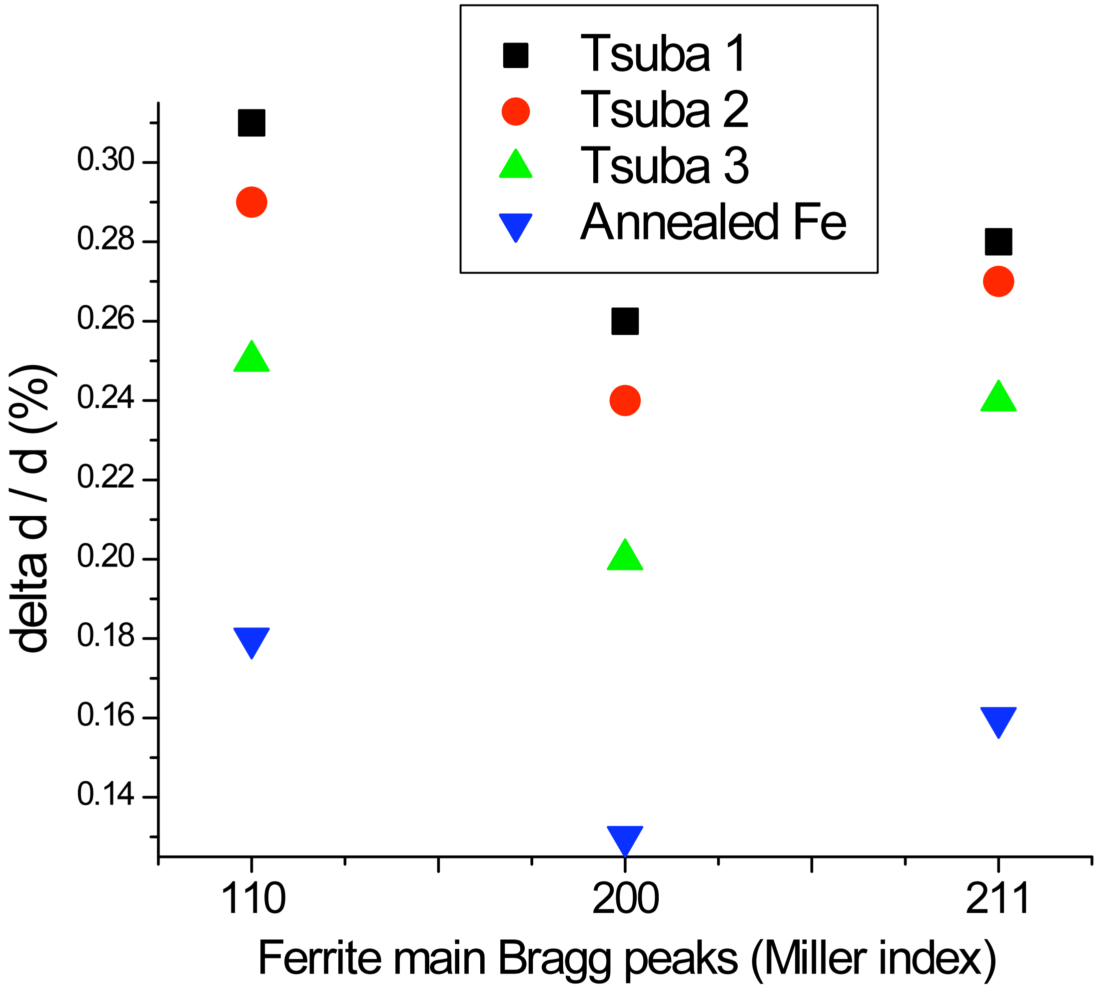
T1  Carburized and tempered

T3  Carburized

Experiment a)

Diffraction

Peak shape analysis



Thermomechanical Actions

T1: work+quenching

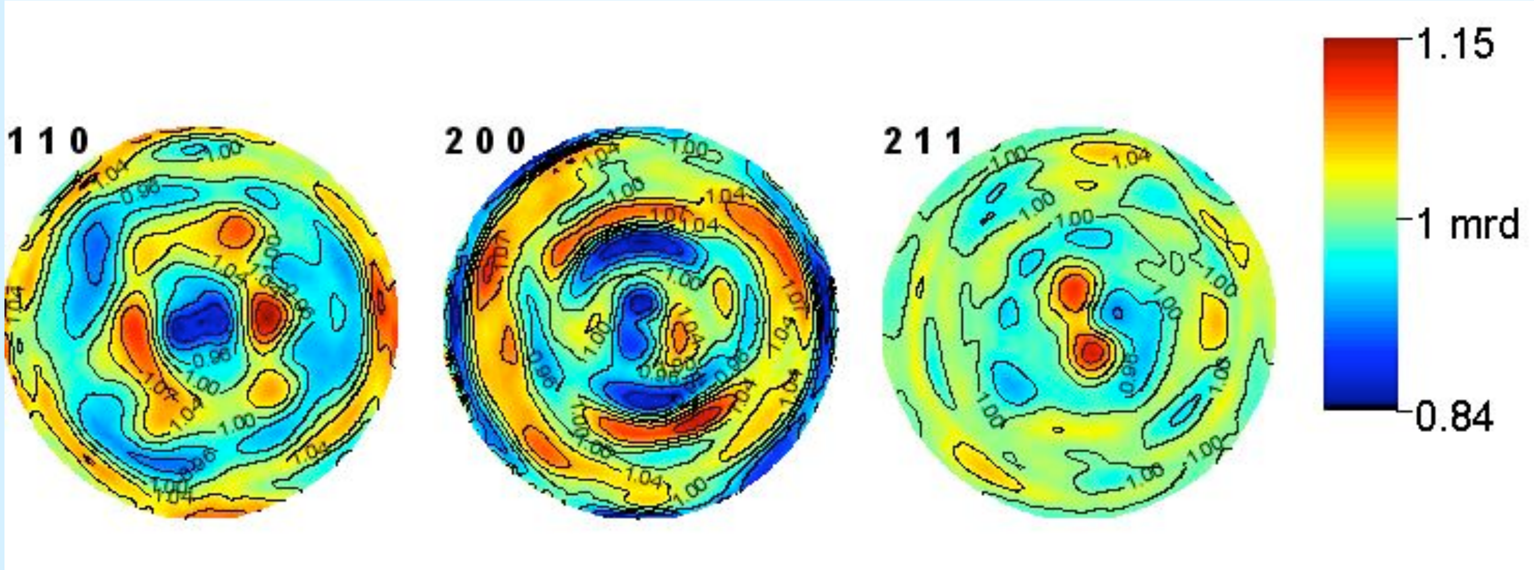
T2: work

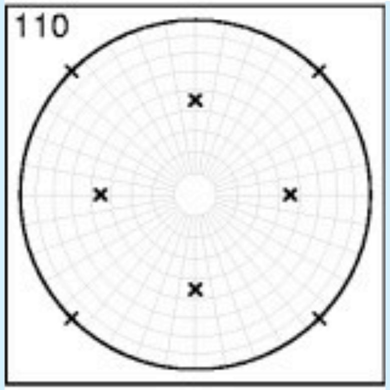
T3: low intensity work or work+annealing

Experiment a)

Diffraction

Texture analysis Tsuba2





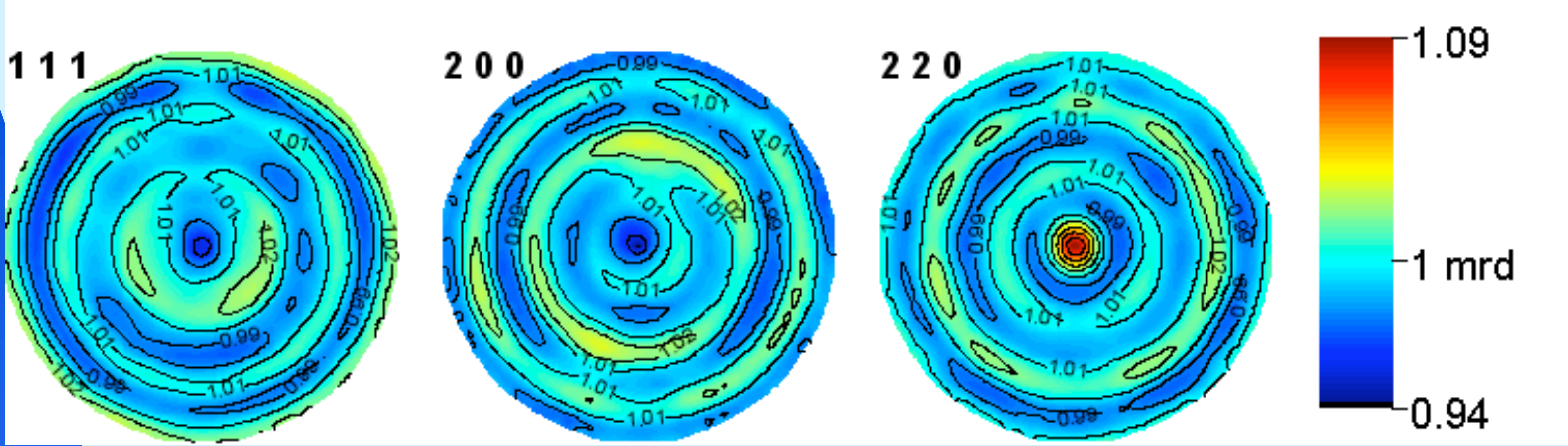
Cube texture:

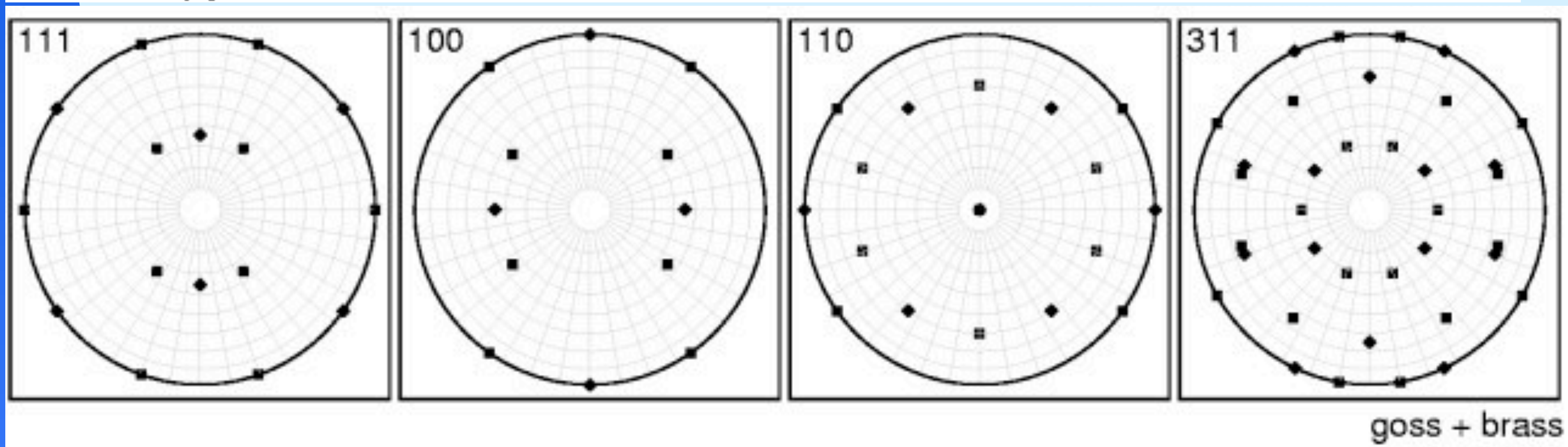
resulting from working without annealing

Experiment a)

Diffraction

Texture analysis Tsuba4





Weak goss-brass texture: resulting from rolling and recrystallization

Experiment b)

Steel sword fragments (Japanese Middle Ages)

Historical remarks

The Japanese style swordsmaking is historically divided in four periods:

Koto (old sword) 987-1596

Shinto (new sword) 1596-1781

Shinshinto (new new sword) 1781-1876

Gendaito (modern era sword) 1876-now

In Koto age the best masterpieces in terms of materials and forging techniques were achieved

Experiment b)

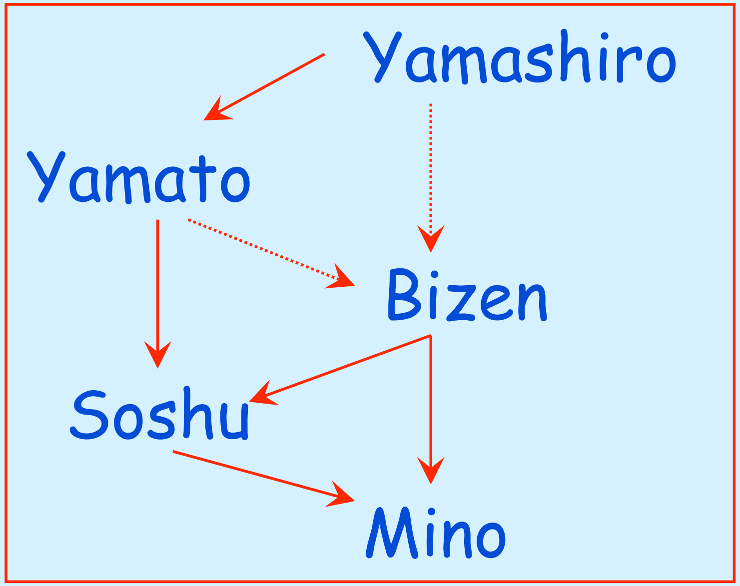
Historical remarks

In Koto age **five** forging traditions were born and cohesisted together

Different smelting and smiting procedures

Different forging techniques

Historical descending of the 5 traditions



Experiment b)

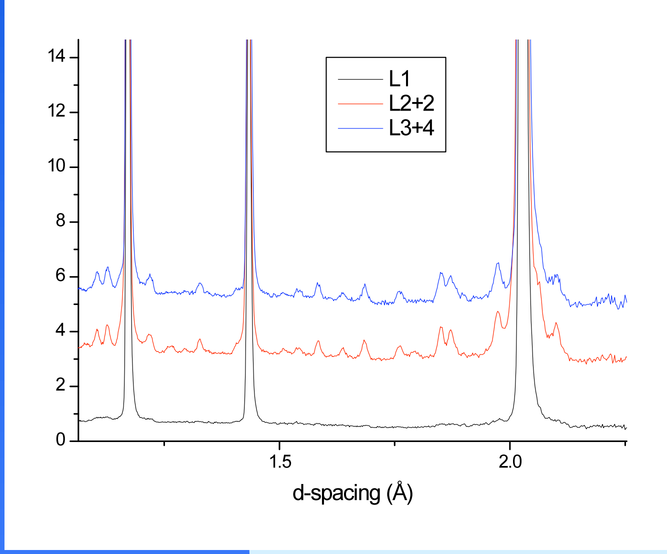
Steel sword fragments (Japanese Middle Ages)

Systematic quantitative analysis of:

5 Koto swords (before 1600)

1 Shinto sword (1600-1800)

1 modern sword (1900)



Carbon content:

Different per different time and different forging tradition

Same for different places and time but same forging tradition

Consiglio Nazionale delle Ricerche

Experiment b) Neutron diffraction results of quantitative analysis

Object	Part	Ferrite (wt%)	Cementite (wt%)	Wuestite (wt%)	Goethite (wt%)	Iron (wt%)	Carbon (wt%)	Tradition or age	Phase distribution considerations
L1	blade	99,13	0,87			99,92	0,08	Gendaito	Very poor carbon
	tang	97,05	2,95			99,79	0,21		
L2	blade	86,5	13,5			99,08	0,92	Shinto	High carbon: evolution of L3
	tang	84,4	15,6			98,94	1,06		
L3	blade	89,88	10,12			99,31	0,69	Koto Bizen	Original Bizen region, high carbon, higher than other blades of the same tradition
	tang	87,75	12,25			99,16	0,84		
L4	blade	99,3	0,7			99,94	0,06	Koto Bizen	Poor carbon same as L5 and L7: typical of derivate Bizen schools?
	tang	98,11	1,89		0,68	99,86	0,14		
L5	blade	97,8	2,2			99,84	0,16	Koto Bizen	Poor carbon same as L4 and L7: typical of derivate Bizen schools?
	tang	99,04	0,96	0,28		99,92	0,08		
L6	blade	94,03	5,97			99,58	0,42	Koto Mino	Medium carbon content
	tang	94,96	5,04		0,25	99,65	0,35		
L7	blade	98,72	1,28	0,57		99,90	0,10	Koto Bizen	Poor carbon same as L4 and L5: typical of derivate Bizen schools?
	tang	98,99	1,01	0,25		99,91	0,09		

Experiment b)

Peak shape analysis for determination of stress levels induced by forging, quenching and tempering

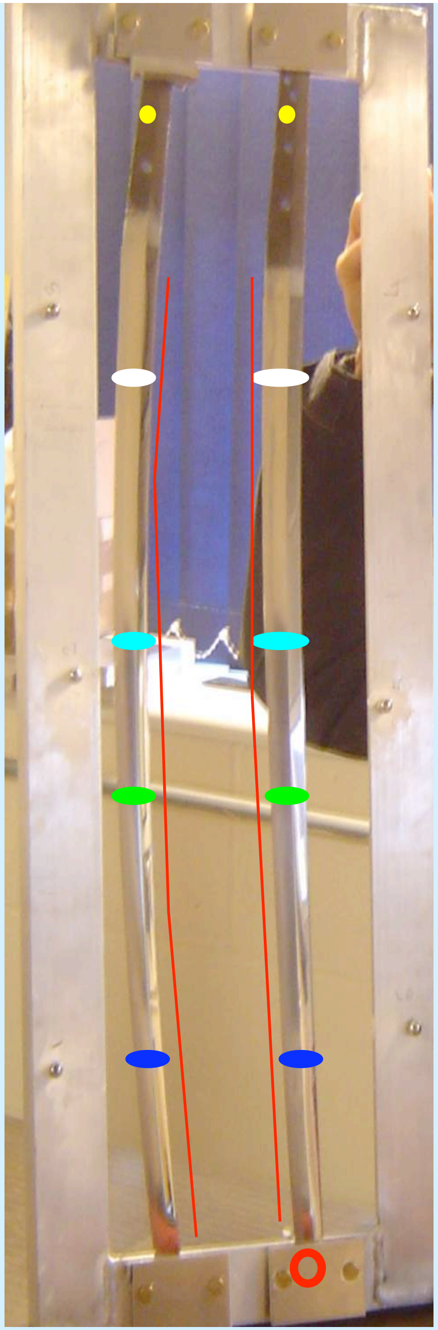
Characteristics			Analysis result	
Area	Blade	position	Width category	Stress level and inner comparison
Gendaito from Mino	1	tang	XXX	High stress, same stress level
		blade	XXX	
Shinto from Bizen	2	tang	XXX	Very high stress, blade much more stressed than tang
		blade	XXXXX	
Koto Bizen from Bizen	3	tang	XXXX	Very high stress, same stress level
		blade	XXXX	
Koto Bizen not from Bizen region	4	tang	XX	Medium stress, same stress level
		blade	XX	
	5	tang	XX	Low-Medium stress, blade less stressed than tang
		blade	X	
Koto Mino	6	tang	XXXXX	Very high stress, tang much more stressed than blade
		blade	XXX	
Koto Bizen not from Bizen region	7	tang	XX	Medium stress, same stress level
		blade	XX	

Experiment e)

Quantitative phase analysis
and strain distribution mapping
on two Koto age blades
Through neutron diffraction.

Searched phases:

ferrite,	cementite,
martensite,	goethite,
wuestite,	magnetite,
hematite,	fayalite,
iron phosphate,	troilite.

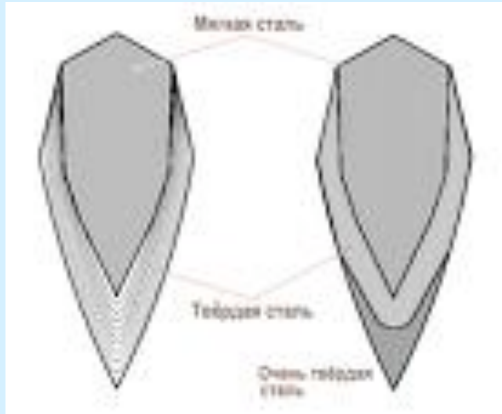


Experiment e)

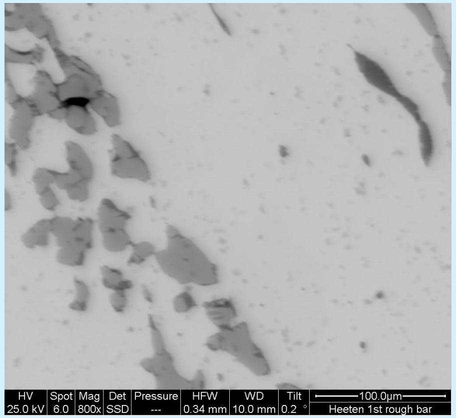
Aims of the measurements (1)

Non invasive quantitative analysis:

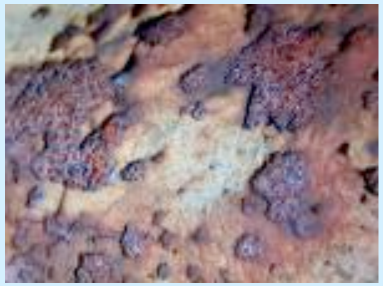
Steel quality (quantification of ferrite, cementite, martensite in different parts)



Slag inclusions



Health status



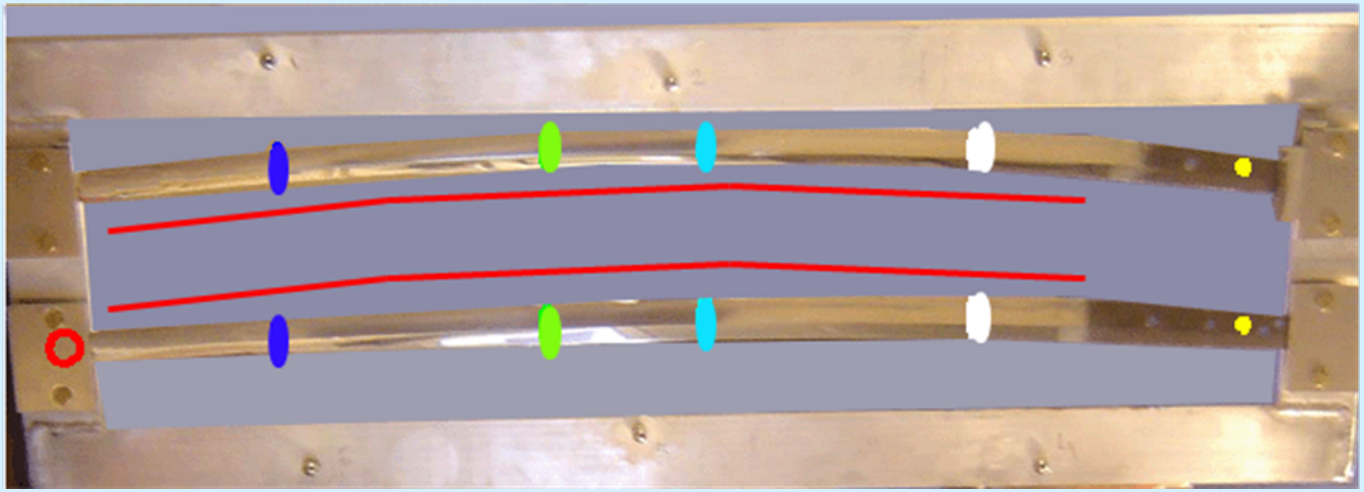
Specials: I.e. is the Yamashiro tip (boshi) original?

Experiment e)

Aims of the measurements (2)

Strain map

1. cross sections mapping
2. edge and ridge mapping
3. evidencing differences in forging methods
4. quantifying the curvature induced by quenching



Experiment e)

Blade n.1: Yamashiro tradition

- Tachi blade
- Sue-Aoe school (end 15th Century)
- Bitchu province
- Low curvature
- Deeply shortened
- Many polishing

Experiment e)

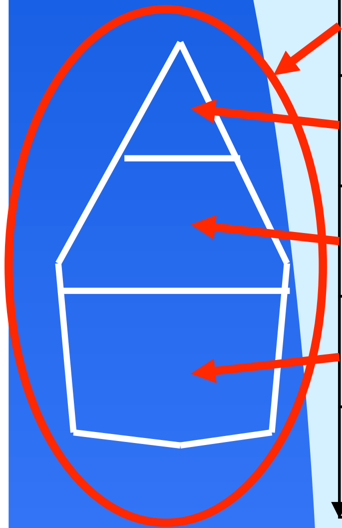
Blade n.2: Mino tradition

- Katana blade
- Kanesada school (half 16th Century)
- Mino province
- High curvature
- Original length
- Many polishing

Experiment e)

Quantitative multiphase analysis results

Yamashiro Aoe blade

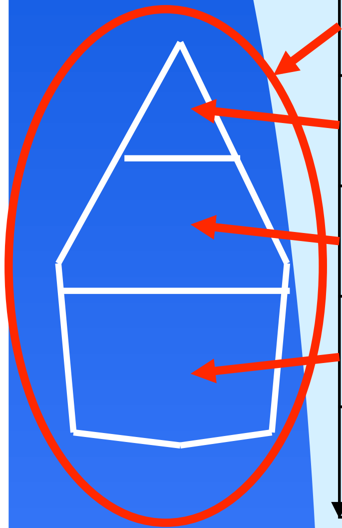


Position	Details	Steel phases and carbon (wt%)			
		ferrite	cementite	martensite	carbon
Boshi	Average	94.8	4.4	0.8	0.29
Monouchi	Average	96.9	2.8	0.3	0.19
Monouchi	Edge	91.3	7.4	1.2	0.50
Monouchi	Core	94.6	4.6	0.8	0.31
Monouchi	Ridge	97.2	2.3	0.5	0.16
Nakago	Average	98.2	1.5	0.3	0.10

Experiment e)

Quantitative multiphase analysis results

Yamashiro Aoe blade

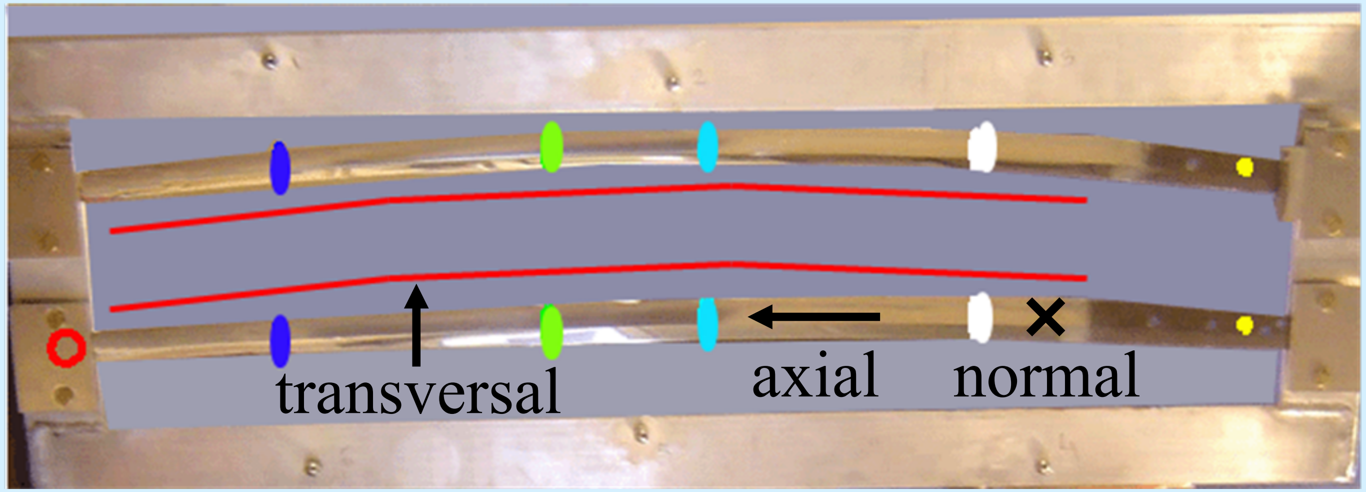


Position	Details	Slag inclusions, corrosions, etc. (wt%)			
		goethite	hematite	fayalite	troilite
Boshi	Average	nil	nil	nil	1.2
Monouchi	Average	0.4	nil	0.5	0.2
Monouchi	Edge	nil	nil	nil	2.0
Monouchi	Core	0.5	nil	nil	1.2
Monouchi	Ridge	0.4	nil	0.5	nil
Nakago	Average	0.3	0.5	0.6	0.5

Consiglio Nazionale delle Ricerche

Experiment e)

Strain mapping

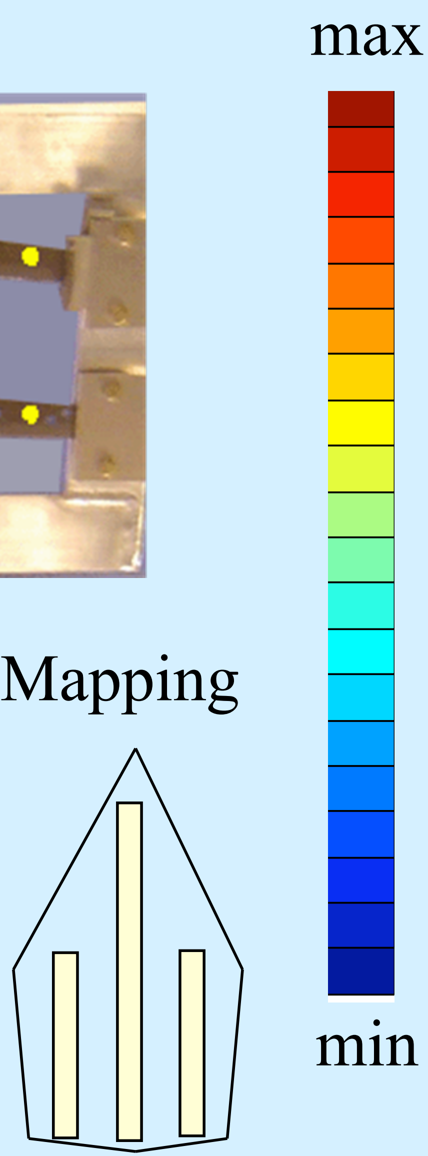


Gauge volumes:

Axial, Normal: 2x2x2 mm^3

Transversal: 2x2x10 mm^3

Mapping

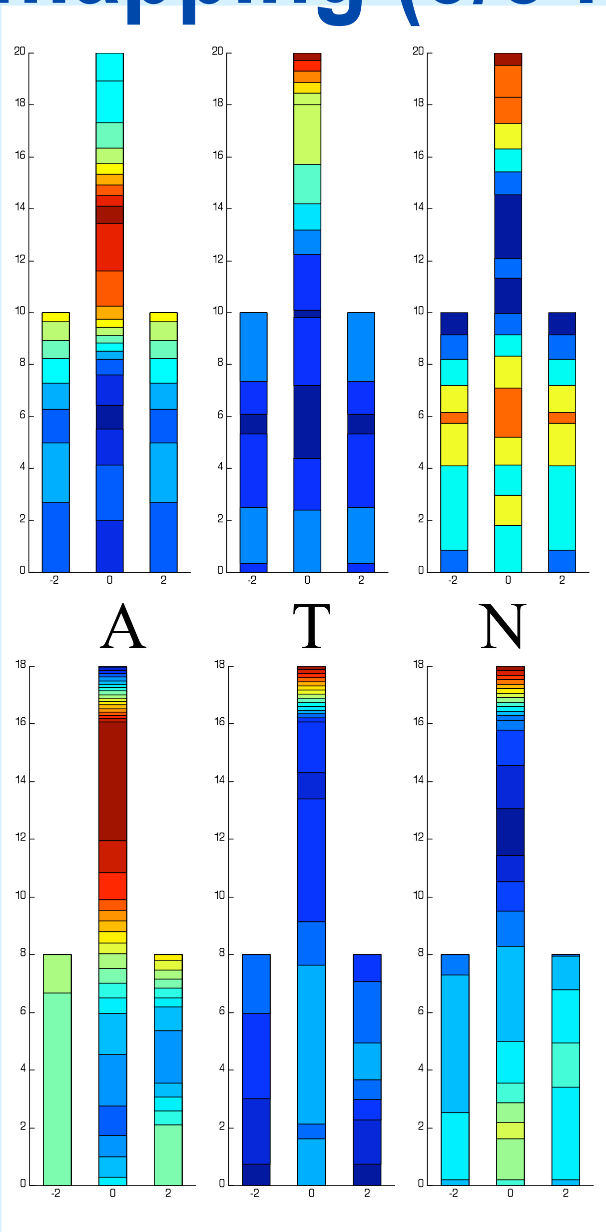


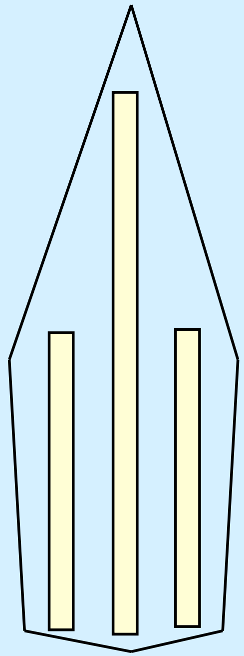
Experiment e)

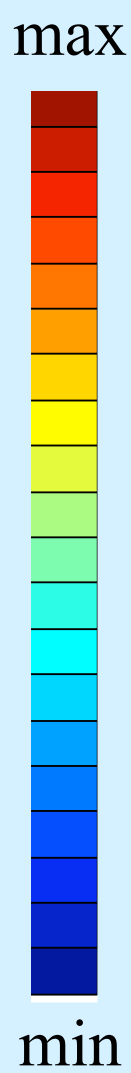
Strain mapping (3/8 length)

Aoe - Yamashiro

Kanesada - Mino



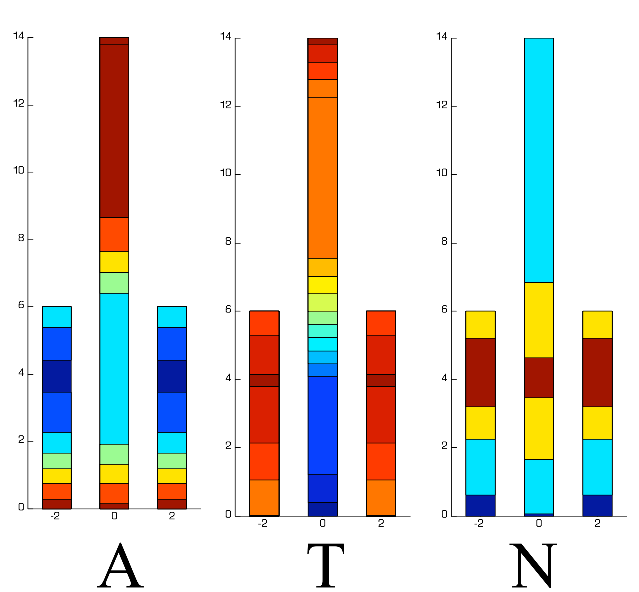


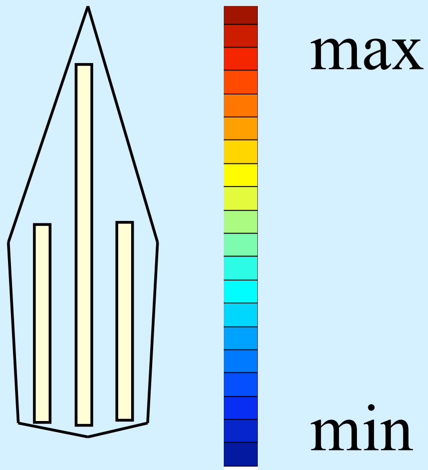


Experiment e)

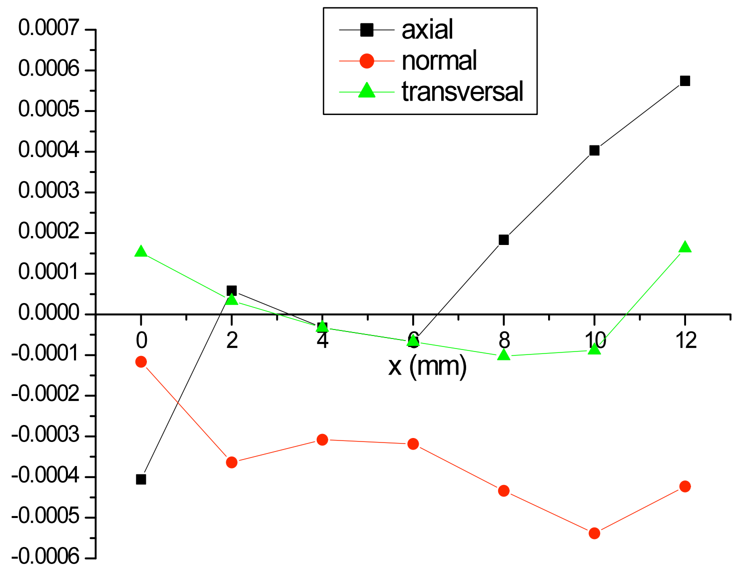
Strain mapping monouchi

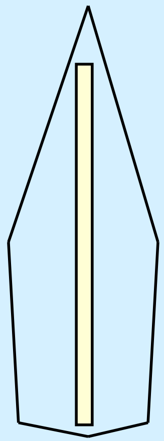
Aoe - Yamashiro





Kanesada - Mino





INES access

- The instrument is funded by CNR
- Web submission of experimental proposals
- 2 deadlines to present proposals (april 16th, october 16th)
- Proposals evaluated by an international panel of experts
- Beam time is assigned
- Experiments can be performed

Website to submit proposals:

http://www.isis.rl.ac.uk/applying/index.htm

INES website:

http://www.fi.isc.cnr.it/ines

Thank you

Consiglio Nazionale delle Ricerche