Application to Cultural Heritage I-Diffraction

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

Presentation Outline:

- **What is archaeometry**
- **Why Neutrons and Neutron Diffraction?**
- **Properties measured through Neutron Diffraction**
- **An example of what we can achieve with ToF - Nd**

What is Archaeometry

Archaeometry consists of the application of scientific techniques to the analysis of archaeological materials

Typical Archaeometry questions:

- **How was it done? (technological knowledge and manufacturing techniques)**
- **When was it done? (datation)**
- **Where was it done? (geographical localization)**
- **How is the object conservation status?**
- **Is the artefact authentic?**
- **Where should we dig?**

<u>A fundamental request: analysis through non destructive techniques!!!</u>

Neutron for Archaeometry

- **All crystalline material – metal, pigments, rock, ceramics – can be analysed by neutron diffraction**

- **Neutrons are an invaluable tool to analyse precious archaeological objects: they are non-destructive and can penetrate deep into the cultural artefact or beneath the surface of paintings, to reveal structures at the microscopic scale, phase composition or provide 3D images of the inner parts of the artefacts**

- **whole artefacts can be placed in the neutron beam and analysed at room conditions, without sample preparation**

Neutron for Archaeometry

Neutron - matter interaction is weak

- **We measure bulk properties**
- **We measure average properties**
- **Scattering volumes can be selected on mm scale**

- **Samples do not need preparation (neutron measurements are non destructive)**

Neutron for Archaeometry

- **Neutrons are expensive and not easily available**
- **Objects need to be transported and stored safely**
- **Interaction of neutrons is weak therefore we need long measuring time (hours)**
- **Scattering volumes can be selected on mm scale**
- **Activation**

Neutron for Archaeometry

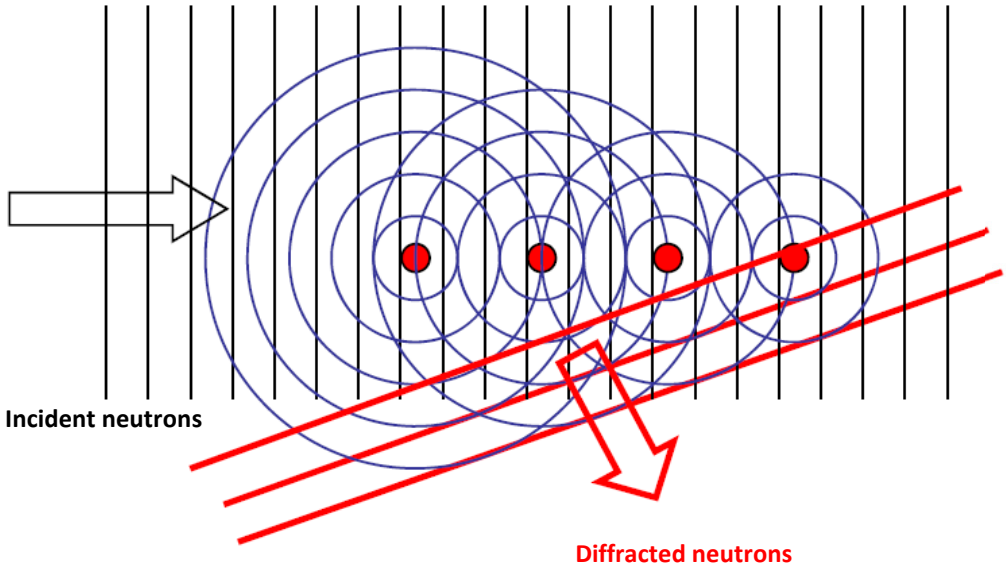
Archaeological object in most cases can be considered randomly oriented polycrystalline material

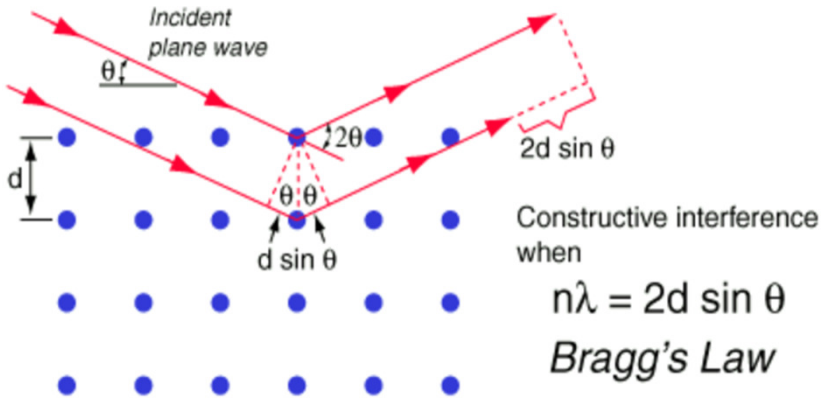
The wavelenght of thermal neutron (E~25 meV) is ~ 1.8 Å, the same order of magnitude of interatomic distances in solids, therefore the structure of solids can be studied by means of the diffraction of thermal neutrons

Thermal Neutron Powder diffraction is our choice !!!

Thermal Neutron Diffraction

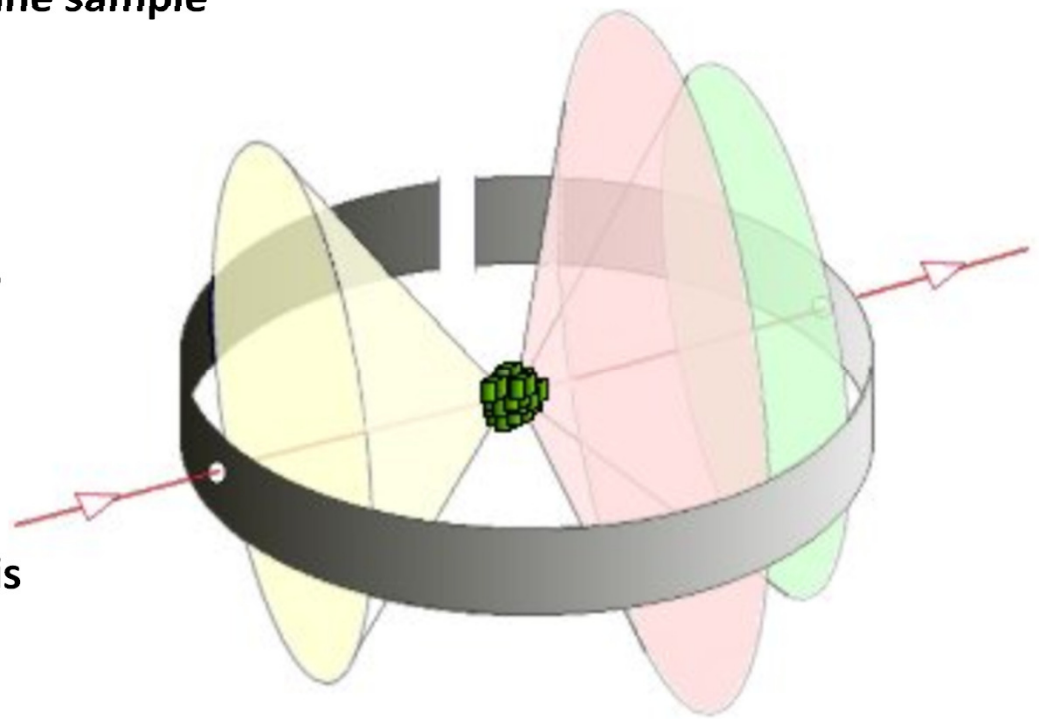
- **The diffraction figure obtained reflects the positions of atoms in solids**
- **Coherent interference occurs when Bragg's law is satisfied**





Neutron Powder Diffraction

- **A randomly oriented polycrystalline sample (e.g. a powder) contains a very large number of crystallites.**
- **A beam impinging on the sample will find a representative number of crystallites in the right orientation for diffraction**
- **Diffraction occurs only at specific angles, those where Bragg's Law is satisfied.**



Time of Flight Neutron Diffraction

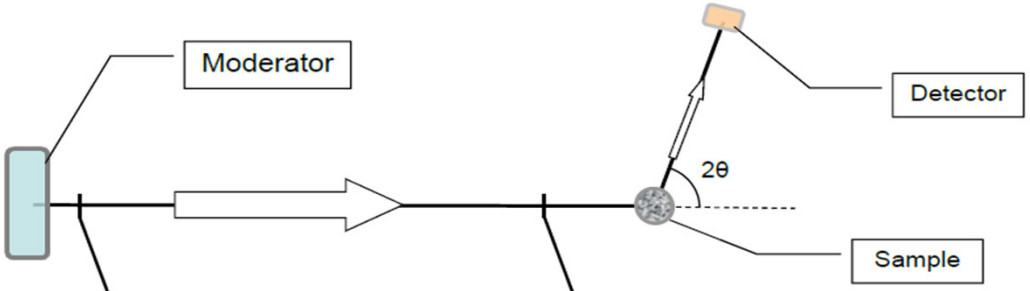
ToF equation:

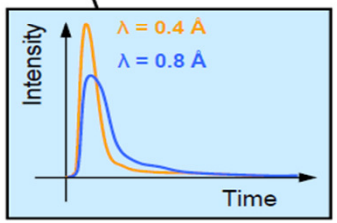
$$d(\text{Å}) = \frac{h}{2m_n}\frac{t(\mu s)}{L(m)\sin\Theta} = \frac{1}{505.56}\frac{t(\mu s)}{L(m)\sin\Theta}$$

Time of flight

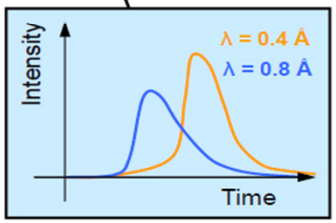
Distance

Scattering angle





The initial pulse from the moderator contains all neutron wavelengths



As they travel down the instrument the faster shorter wavelength neutrons arrive first

Time of flight diffractometers

- The neutrons are sorted by time at the sample and the diffraction done as a function of time
- A full diffraction pattern is collected at a fixed angle

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**

Rietveld refinement

What can be Rietveld refinement tell us from our Neutron Diffraction data?

- **Phase composition**
- **Lattice parameters**
- **Peak shape analysis**
- **Texture**

Rietveld refinement

- **The idea behind Rietveld refinement is to minimize the difference between measured and calculated intensities collected at various θ.**
- **It is a multiparameter fit, and the parameters we fit are related with physical properties of our samples**
- **Intensities of Bragg peaks at a specific θ are related with the relative amount of phases present in the sample and presence of texture**
- **Position of the Bragg reflection is related with lattice parameter and diffractometer characteristcs**
- **Broadening of Bragg reflection is related with presence of microstrain and grains size. Bragg reflections are usually described in terms of Gaussian and Lorentzian conponent**

Software for Rietveld refinement

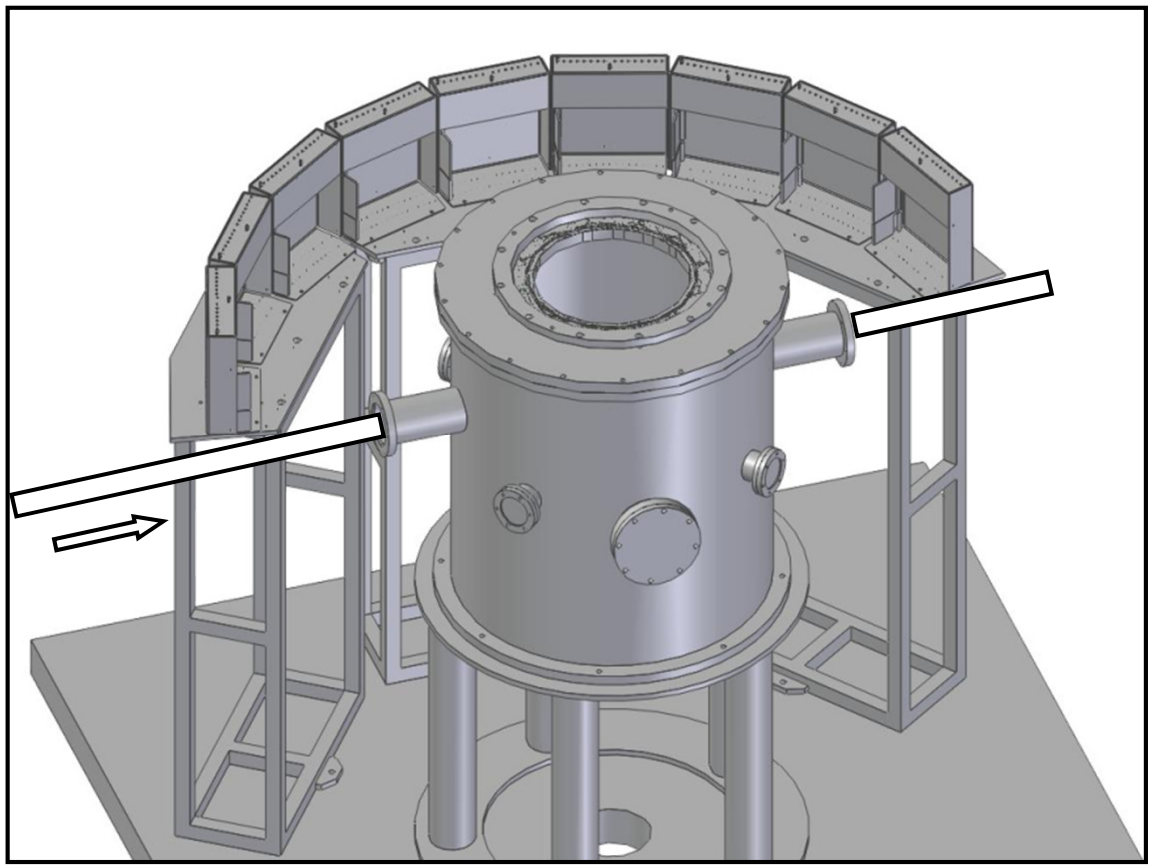
- **GSAS: most used; very good for crystal structure refinement and TOF neutron; not easy to use but there is a lot of knowledge around. A friendly graphical interface available with Expgui.**

- **FullProf: best for magnetic materials; good for crystal structure refinements;**

- **Maud: for material scientists; reasonably good for quantitative phase analysis, size-strain and texture. Best in the case of texture/strain problems. Come with a graphical user interface.**

GSAS most of the times, Maud for texture analysis

Italian Neutron Experimental Station
INES@ISIS

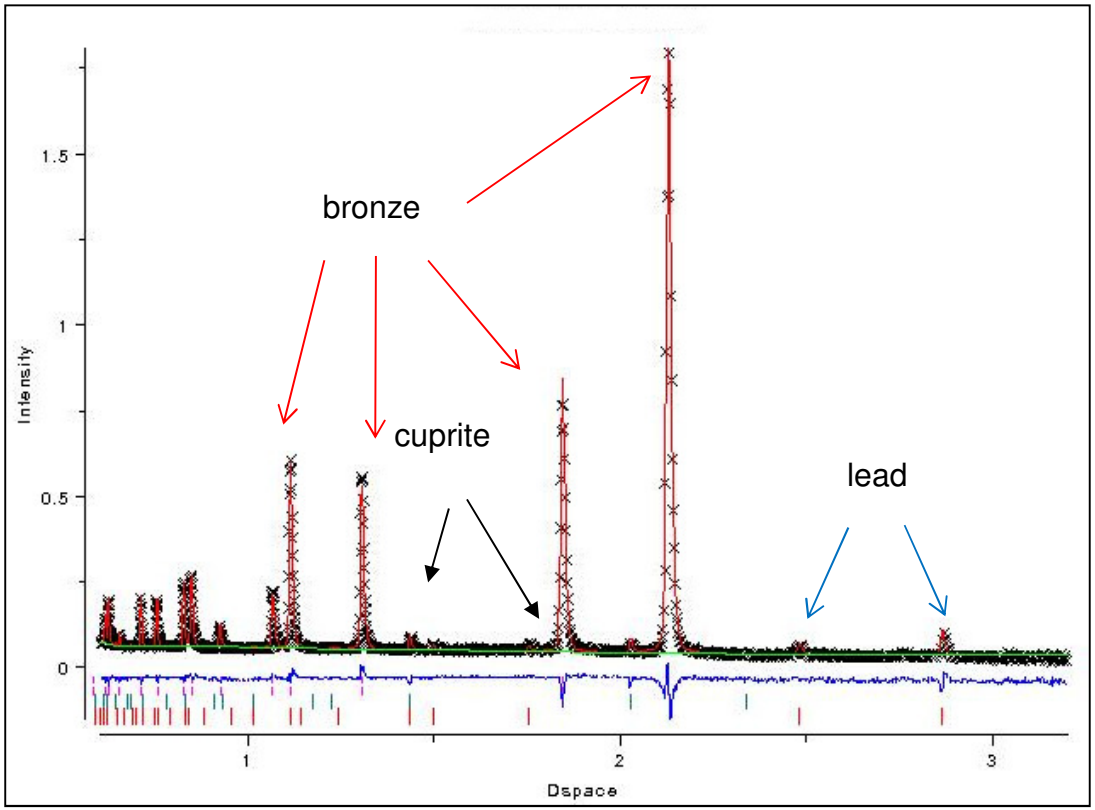


Italian Neutron Experimental Station

- Large sample holder tank (1 m^3)
- 144 diffraction detectors
- 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
- NRCA - YAP detector

Phase composition

Rietveld Refinement



Quantitative multiphase analysis
→ determination of the weight fraction of the phases composing the sample

The sample is made of bronze, leaded bronze. Corrosion products (cuprite are present in small amount)

Elemental composition of a single phase binary metal alloy

- **Vegard's law is an approximate empirical rule which holds that a linear relation exists, at constant temperature, between the crystal lattice parameter of an alloy and the concentrations of the constituent elements**

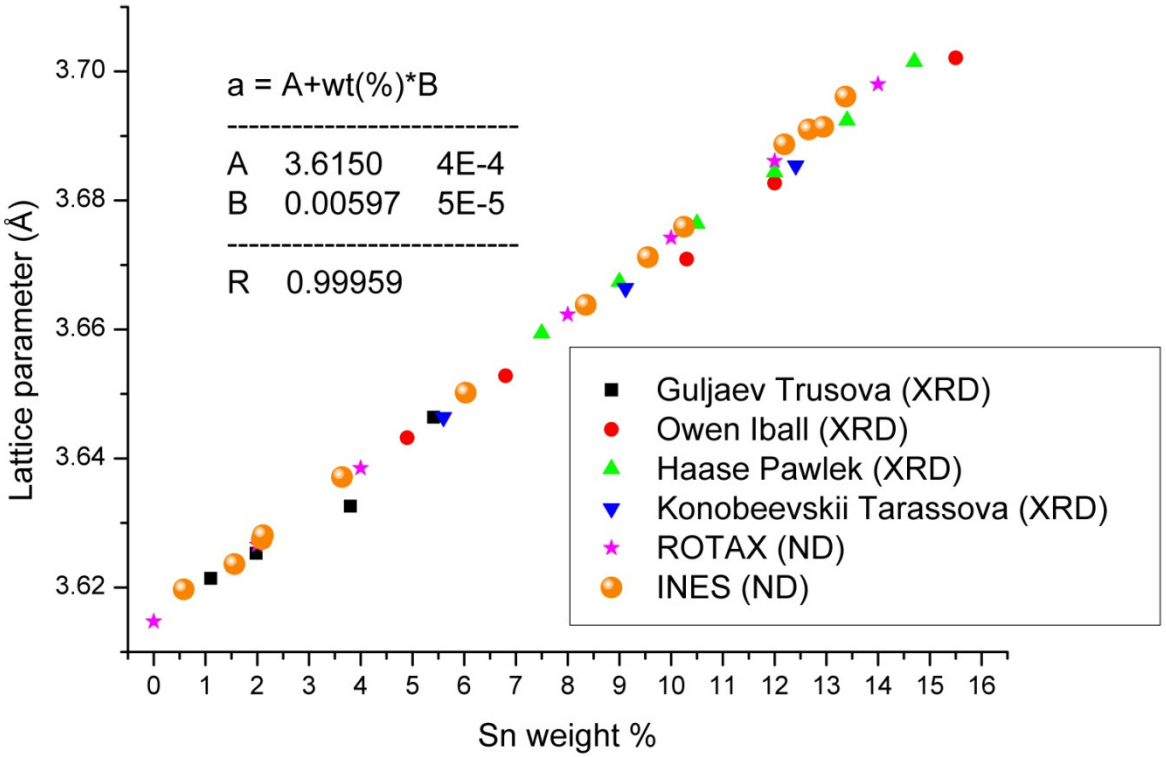
- **We can measure lattice parameter of a binary alloy and derive the elemental composition, if we have a calibration curve**

- **Despite the sensitivity of the method being lower than other traditional analysis, it allows segregation and corrosion problems to be overcame (high reliability)**

- **It is a non destructive method to derive the chemical composition of a binary alloy!**

Elemental composition of a single phase metal alloy

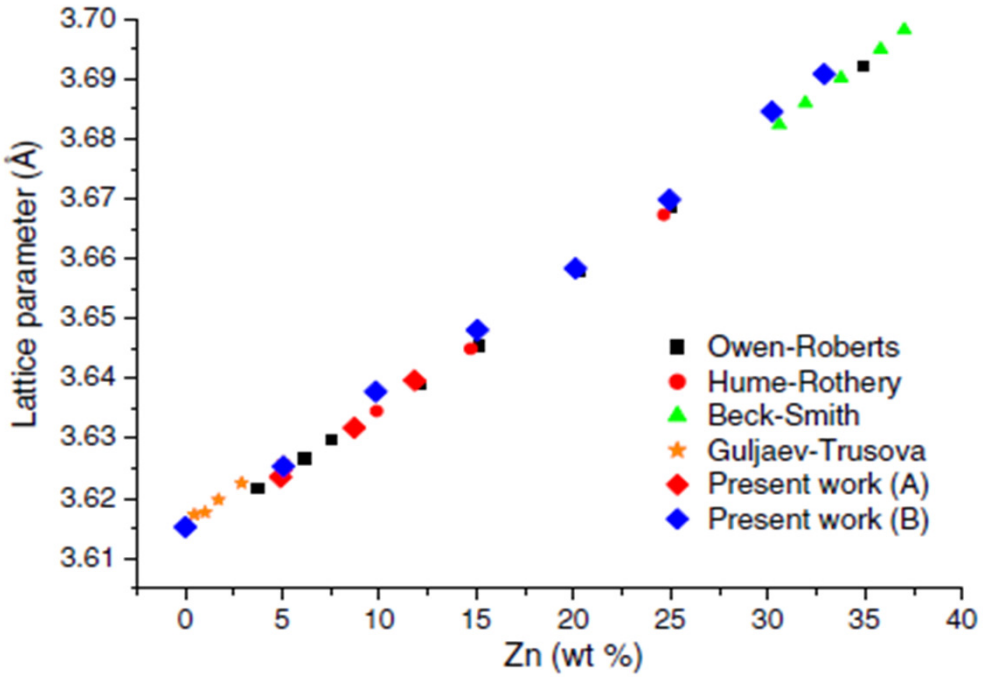
Bronze (Cu, Sn), widely used in antiquity



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

Elemental composition of a single phase metal alloy

Brass (Cu, Zn), widely used in antiquity

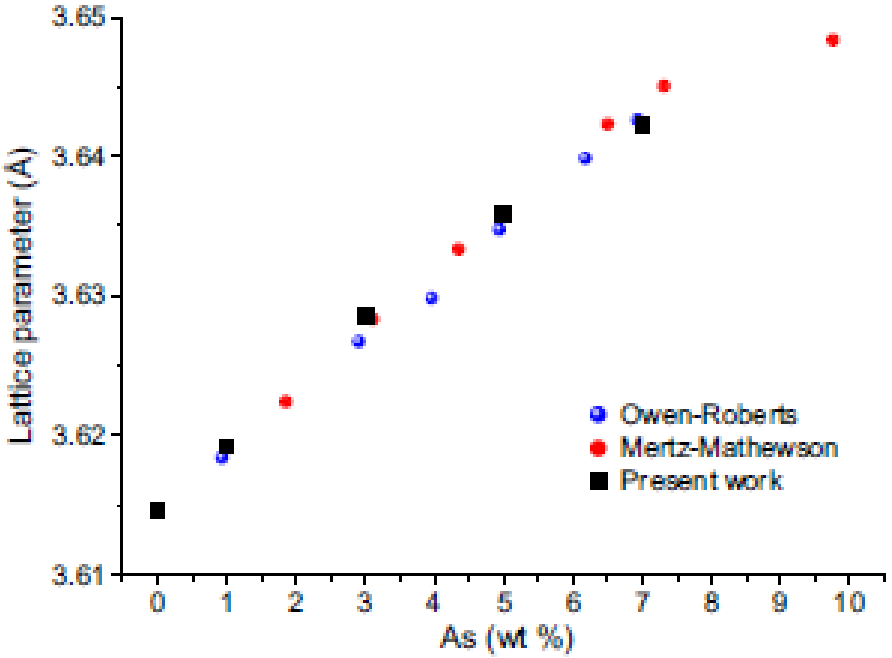


Lattice parameter determination through Rietveld refinement of samples of known composition allowed us to build reliable calibration curve

Now we can derive mesuring the lattice parameter of Cu phase in our objects!!!!

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

Materials characteristics effects on Powder Diffraction

- **Peak broadening due to Grain size and Residual Stress (Strain)**
- **Change in peaks intensity due to preferred orientation (texture)**

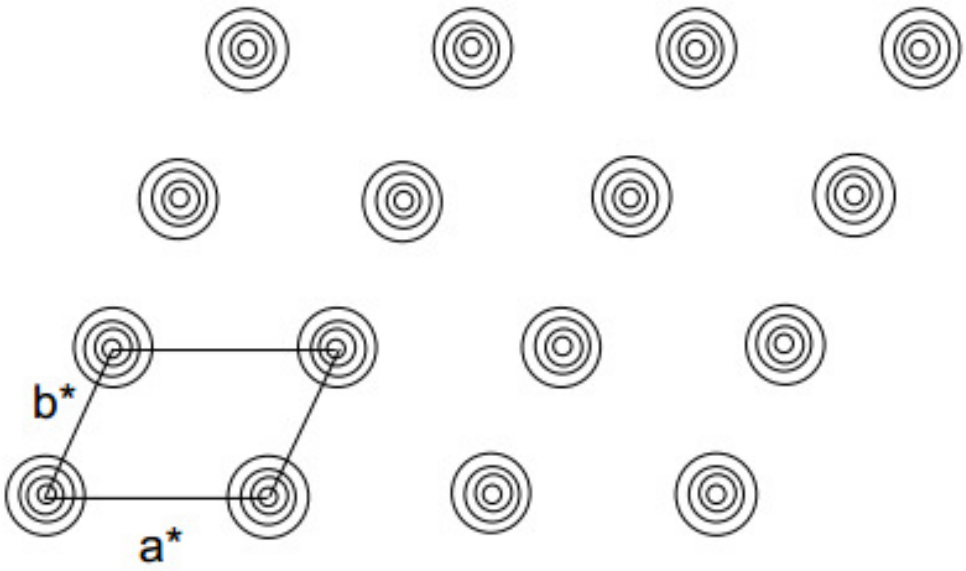
Crystallite Size Broadening

The Fourier transform (FT) from an infinite array of regularly spaced objects is an array of delta functions.

The FT from a finite length array is broadened.

The finite sizes of crystallites will broaden all orders of reflections equally in units of Q ($\propto$ d*)

- differing reciprocal space directions may have differing amounts of broadening, if crystallites dimensions are not isotropic on average



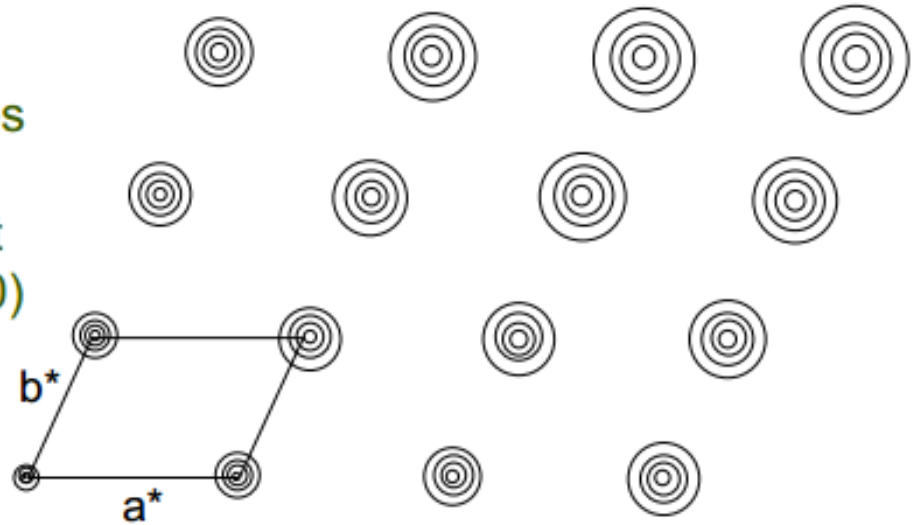
Crystallite Size Broadening can produce Lorentzian peak shapes (common) or Gaussian peak shapes (uncommon) or a combination of both.

Microstrain Broadening

When a material has residual stresses present, some crystallites are compressed. This must be balanced by other crystallites that are stretched (because $\sum F=ma=0$)

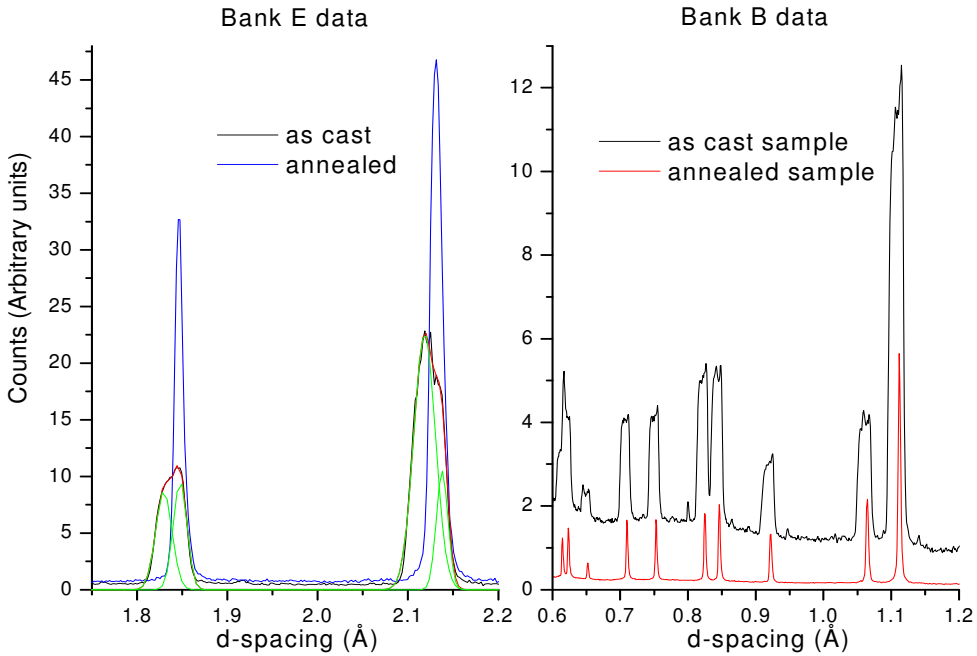
This leads to a range of lattice constants.

The spread between diffraction locations for the maximum and minimum lattice constant increases linearly with Q ($\Delta Q/Q$ or $\Delta d/d$ = constant)



Peak shape analysis

Bronze standard measured on INES



- **broadening due to non directional internal residual microstrain i.e. defects: Gaussian behaviour (S_{400} parameter in cubic systems)**
- **broadening due to small crystallographic domain size (mosaicity): Lorentzian behaviour (γ_2)**
  Domain size: $d=K_s/\gamma_2$

Diffraction peak sub-structure comes from lattice parameter distribution in an inhomogeneous alloy (dendrites)

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

Japanese helmet of 16th and 17th century

sample 1

sample 2

sample 3

sample 4

sample 5

sample 6

sample 7

sample 8

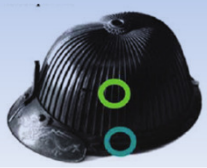
Japanese helmet of 16th and 17th century

In collaboration with Stibbert Museum in Florence, the Wallace collection in London and a British private collector

Quantitative phase analysis

- degree of carbon content in the alloy
- conservation status (corrosion products not visible since the helmets are lacquered)
- efficiency of the extracting process of iron from the ore (amount of oxides as wuestite, magnetite and hematite not completely reduced)
- Manifacturing techniques

Japanese helmet of 16th and 17th century



Meas. point	Ferrite (wt%)	Cementite (wt%)	Wüstite (wt%)	Goethite (wt%)	Magnetite (wt%)	Hematite (wt%)	Fayalite (wt%)	Troilite (wt%)
1A	96.8 ± 0.1	0.8 ± 0.1	0.2 ± 0.1	0.2 ± 0.1	0.4 ± 0.1	0.3 ± 0.1	0.4 ± 0.1	0.9 ± 0.1
1D	95.5 ± 0.2	1.4 ± 0.2	Traces	1.2 ± 0.2	0.5 ± 0.1	0.6 ± 0.1	—	0.8 ± 0.2
2A	91.4 ± 0.1	5.6 ± 0.1	0.7 ± 0.1	Traces	1.5 ± 0.1	—	—	0.8 ± 0.1
2D	92.1 ± 0.2	3.3 ± 0.2	1.0 ± 0.1	Traces	2.2 ± 0.1	—	0.5 ± 0.1	0.9 ± 0.1
3B	99.0 ± 0.1	—	0.3 ± 0.1	0.5 ± 0.1	Traces	0.2 ± 0.1	—	—
3D	98.2 ± 0.3	—	Traces	0.9 ± 0.3	—	Traces	0.9 ± 0.3	—
4B	99.2 ± 0.1	—	0.2 ± 0.1	0.6 ± 0.1	—	—	—	—
4D	96.1 ± 0.1	1.6 ± 0.1	0.1 ± 0.1	0.9 ± 0.1	—	0.5 ± 0.1	—	0.8 ± 0.1
5B	96.7 ± 0.2	1.0 ± 0.1	0.3 ± 0.1	0.2 ± 0.1	0.4 ± 0.1	0.4 ± 0.1	—	1.0 ± 0.2
5C	97.4 ± 0.2	—	Traces	1.7 ± 0.1	0.1 ± 0.1	0.4 ± 0.1	Traces	0.4 ± 0.2
5E	98.1 ± 0.2	1.1 ± 0.1	—	Traces	—	0.4 ± 0.1	—	0.4 ± 0.2
6B	99.1 ± 0.1	0.4 ± 0.1	0.1 ± 0.1	0.4 ± 0.1	Traces	—	—	—
6C	97.9 ± 0.3	1.5 ± 0.2	—	—	0.2 ± 0.1	—	—	0.4 ± 0.3
7Ab	97.8 ± 0.2	1.1 ± 0.2	0.4 ± 0.1	—	0.4 ± 0.1	0.3 ± 0.1	—	—
7Ac	97.0 ± 0.2	1.2 ± 0.2	0.4 ± 0.1	0.3 ± 0.1	0.2 ± 0.1	0.2 ± 0.1	—	0.7 ± 0.1
7At	97.1 ± 0.2	0.7 ± 0.1	0.3 ± 0.1	0.6 ± 0.1	0.3 ± 0.1	0.3 ± 0.1	0.4 ± 0.2	0.3 ± 0.1
7Bb	97.6 ± 0.2	1.3 ± 0.2	0.2 ± 0.1	0.9 ± 0.2	—	—	—	—
7Bc	97.1 ± 0.3	1.4 ± 0.2	0.1 ± 0.1	0.7 ± 0.2	—	0.3 ± 0.1	0.4 ± 0.3	trc
7Bt	96.5 ± 0.2	1.9 ± 0.1	0.2 ± 0.1	0.9 ± 0.2	0.2 ± 0.1	0.3 ± 0.1	—	trc
7Eb	95.5 ± 0.4	2.1 ± 0.3	—	0.2 ± 0.1	0.3 ± 0.2	0.5 ± 0.2	—	1.4 ± 0.4
7Ec	96.1 ± 0.3	2.3 ± 0.3	0.2 ± 0.1	—	Traces	—	—	1.4 ± 0.3
8E	99.1 ± 0.1	—	0.2 ± 0.1	—	—	0.7 ± 0.1	Traces	—

Japanese helmet of 16th and 17th century

- **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

Japanese helmet of 16th and 17th century

- **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 (Fe3O4 and Fe2O3, 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

Japanese helmet of 16th and 17th century

- **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**

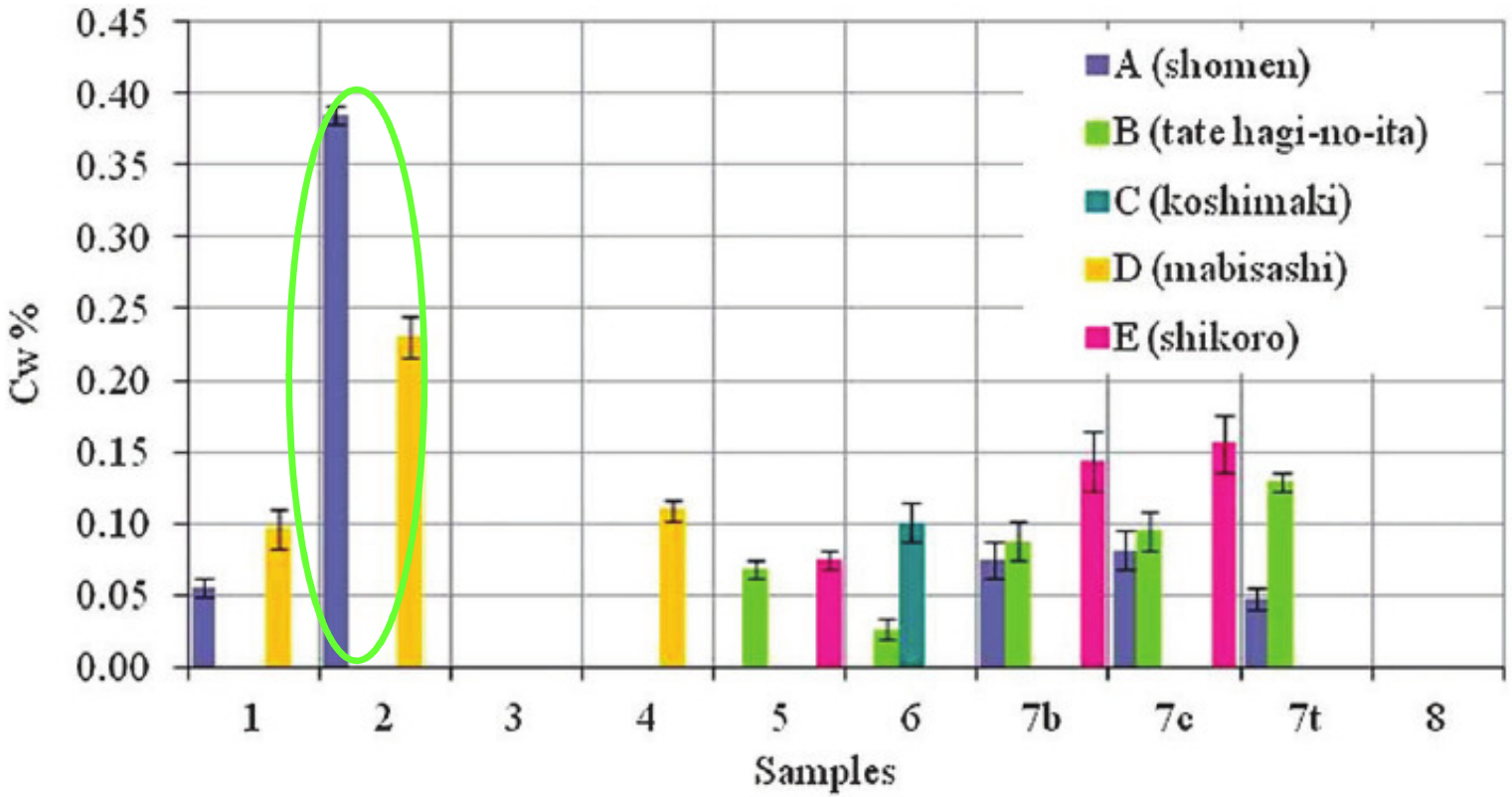
poor conservation status

Japanese helmet of 16th and 17th century

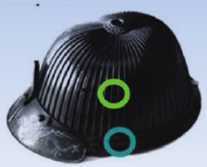
- **Fayalite: this is an iron silicate (Fe2SiO4). It forms during smelting, by the reaction between iron oxides and the rocks where these are embedded, or a possible reaction with the walls of the furnace. Fayalite usually remains trapped inside the bloom, unless liquid iron or steel is formed during 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**

Japanese helmet of 16th and 17th century



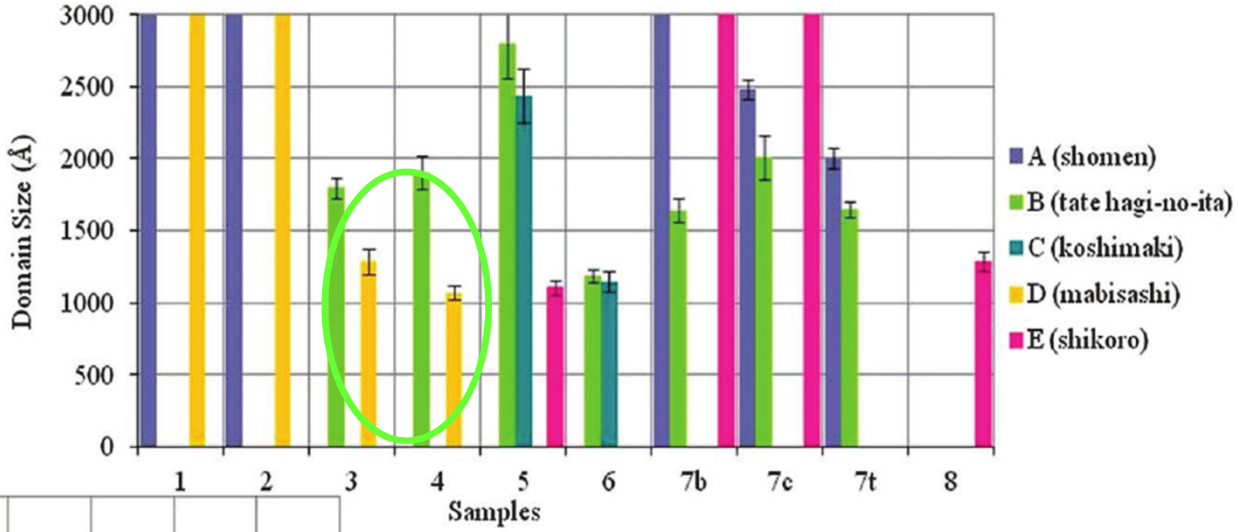
Japanese helmet of 16th and 17th century

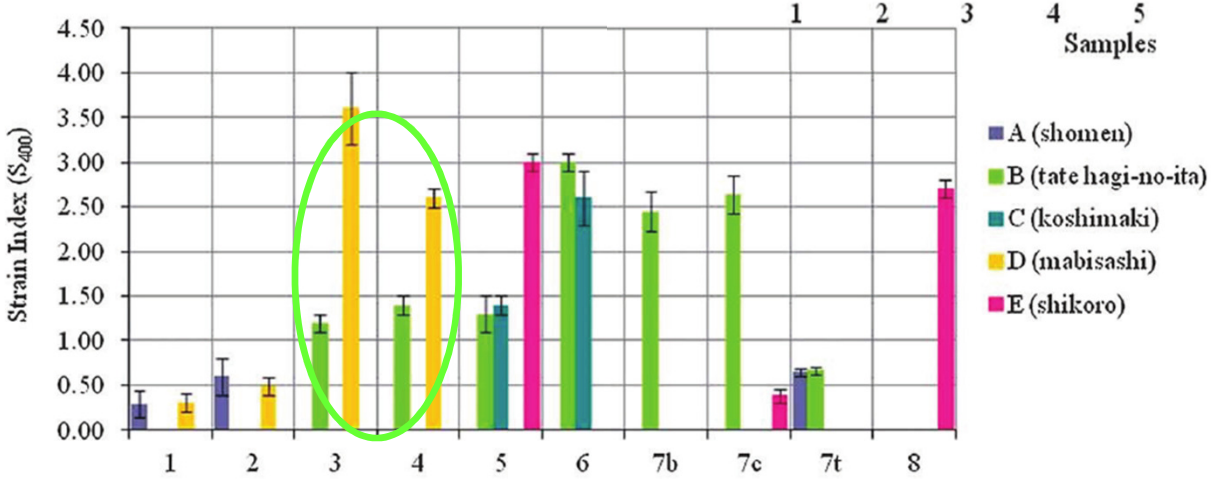


Peak shape analysis:

γ_2

Grain size

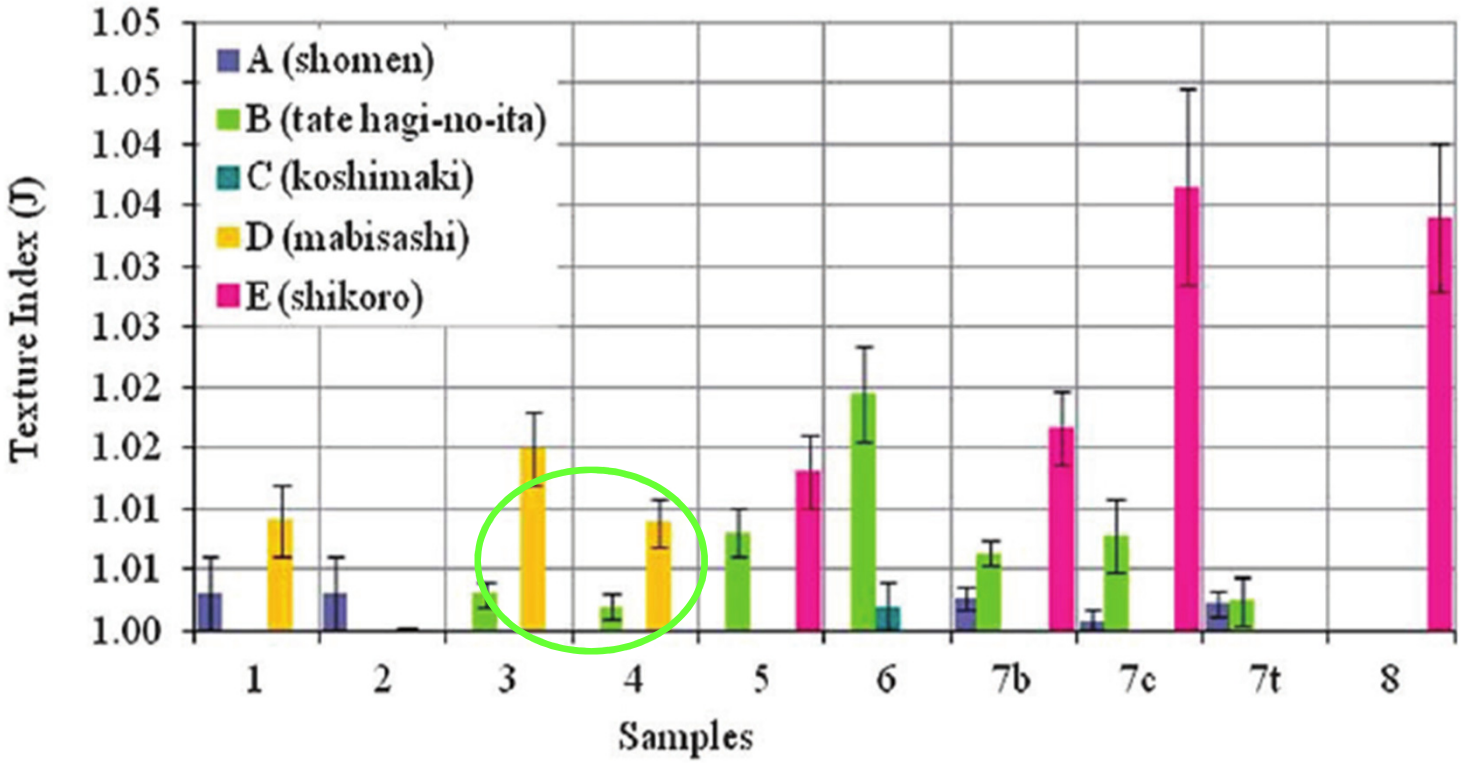




Peak shape analysis: S400 strain

Japanese helmet of 16th and 17th century

Texture index: J



Japanese helmet of 16th and 17th century

- sample no. 3 and no. 4 represent a good example of how Japanese armourers were able to control and reproduce the manufacturing process, obtaining almost an exact copy of the same object
- helmets no. 2 and no. 6 proved to be the two most interesting samples and, in fact, they are the ones that are signed by the armourers
- helmet no. 2 shows the high level of carbon content that Japanese metallurgists could reach
- helmet no. 6, not only stands out for its high aesthetic quality, but also for the high quality of iron
- helmet no.7 is made of high quality iron but is in poor conservation status

Thank you for your attention!