METHODOLOGICAL ASPECTS OF SANS AND TOF NEUTRON DIFFRACTION MEASUREMENTS ON POTTERY. THE CASE OF MISENO AND CUMA

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Length scales

- ~10 µ
- 100-200 nm
- 10-20 nm
- < 1 nm

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Some questions

Is it possible to use neutron instruments for investigating pottery?
- Multiple scattering effects ↔ sample thickness
- Non destructivity vs. micro destructivity
- Activation

Which are the firing parameters neutrons are sensitive to?
- Maximum firing temperature
- Composition
- Heating rate

The application of neutron techniques to an actual case gives information?
- The case of Miseno and Cuma

Which are the prospects opened by this approach?
Facilities

Forschungszentrum jülich
KWS I - KWS II - KWS III - DKD reactor

Laboratoire Léon Brillouin
PAXE - PAXY reactor

Rutherford Appleton Laboratory
ROTAX – VESUVIO - INES spallation
D \sim 1 \times 10^{-1} - 2 \times 10^3 \text{ Å}

q = |\vec{q}| = \frac{4\pi}{\lambda} \sin \left( \frac{\theta}{2} \right)

Velocity selector

collimation

guide

sample

detectors

Up to 20 m
SANS

\[ -\text{Si-O-Si}- \]

\[ < 1 \text{nm} \]

\[ 10-20 \text{ nm} \]

\[ 100-200 \text{ nm} \]

\[ \sim 10 \mu \]

\[ I_q \]

\[ R_g \]

\[ d \]

\[ q \]

\[ 10^{-1} \quad 10^{1} \quad 10^{2} \quad 10^{3} \quad 10^{4} \quad 10^{5} \quad 10^{6} \]

\[ 10^{-3} \quad 10^{3} \quad 10^{5} \quad 10^{7} \]

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The Bragg’s law

\[ n\lambda = 2d \sin \theta \]
ND

- Si-O-Si -

100-200 nm
10-20 nm
< 1 nm

$I \propto q$

$[\text{a.u.}]$

$q$

d-spacing
Is it possible to use neutron instruments for investigating pottery?

- Multiple scattering effects ↔ sample thickness
- Non destructivity vs. micro destructivity
- Activation

The different thicknesses:

- $d \sim 6 \text{ [mm]}$
- $d \sim 3 \text{ [mm]}$
- chips $\sim 0.5 \text{ [mm]}$
- powder
\begin{itemize}
  \item The thinner is the sample the more reliable is the measurement. If possible, a micro-destructive sampling is the best solution.
  
  \item The use of high energy neutrons lowers multiple scattering effects.
  
  \item It is possible to apply numerical corrections.
\end{itemize}
Firing parameters

Which are the firing parameters neutrons are sensitive to?

- Maximum firing temperature
- Composition
- Heating rate

The different firing conditions:

The maximum firing temperature: 650 [°C], 700 [°C], 750 [°C], 800 [°C], 850 [°C], 920 [°C]

The heating rate: a fast and a slow rate

The composition: ‘Terraglia Bianca’ and ‘Terraglia Rossa’
• Between the maximum firing temperature and the parameter \( d \) there is a linear dependence.

• \( d \) does not show any extra dependence (or it is not detectable) on the heating rate.

• The dimension of the voids/aggregates seems to have a linear dependence on the maximum firing temperature but there is incertitude on the result.
Firing parameters

\[ A_{mean} = \left[ \overline{ph_1} = \frac{N}{i=1} \overline{ph_1(i)} / N, \overline{ph_2}, \ldots, \overline{ph_n} \right] \]

If a sample misses some \((n-k)\) crystalline phases then

\[ A_j = \begin{cases} 
ph_{m,j} & \text{if } m < n - k_j \\
0 & \text{if } k_j < m < n 
\end{cases} \]

\[ \delta_j = \sum_{i=1}^{n} \frac{ph_{i,j} - \overline{ph_i}}{\overline{ph_i}} \]

- This analysis shows the differences in the phase content evolution at different temperatures.

- The distance value can be useful to define groups.
During the Roman Age, the harbour of Miseno was the biggest military harbour of the Mediterranean.

conversion into a commercial harbour. It kept its activity until the casting off by the Duchy of Naples in favour of the Aghlabids Arabs from Sicily.

abandoned in the second half of the IX century A.D.

Early typology tends to disappear during the VIII century A.D.; while, other typologies continue until the IX century A.D. and are actually known as "broad line ceramic".
The samples have been found in the same site, called "Località Cudemo", where two kilns have been discovered. The two kilns were never operative at the same time, nevertheless the finds belong to the same typology. The second kiln was indeed constructed on top of the first one after its voluntary burial. In that area, there is no evidence of other facilities after the 9th century A.D.
### Medieval sherds

#### Miseno

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#### Cuma

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Samples from Miseno have a homogeneous composition.

Samples from Cuma are more dispersed.

Samples from Cuma and Miseno have a composition similar to that of the red reference samples.
- The maximum firing temperature lowers moving from the 7th to the 12th century.

- This feature is shared by the samples of Miseno and Cuma.
The application of neutron techniques to an actual case gives information?

- The case of Miseno and Cuma

VI sec. AD — XII sec. AD

TIME

Romans — Aghlabids — Arabs

HISTORY

abandonment

900-1000 °C — 700-800 °C

ROUGHNESS

TEMPERATURE
Outlook

Study on the firing environment: oxidizing and reducing

Better define the mesoscopic structures

Sampling of a wider geographical area

Other typologies of materials
Microscopic structures

$600^\circ C$  $950^\circ C$

$10^{-3}$  $10^{-2}$  $10^{-1}$  $10^{0}$  $10^{1}$  $10^{2}$  $10^{3}$

$q$

$\text{USANS}$  $\text{SANS}$

$T \ [^\circ C]$

$0$  $500$  $1000$  $1500$  $2000$

$0$  $0.5$  $1$  $1.5$  $2$  $2.5$  $3$  $3.5$  $4$

$10^{-3}$  $10^{-2}$  $10^{-1}$  $10^{0}$  $10^{1}$  $10^{2}$  $10^{3}$

$q$

$I$

$q$

$S\text{ANS}$  $U\text{SANS}$

$10^{-3}$  $10^{-2}$  $10^{-1}$  $10^{0}$  $10^{1}$  $10^{2}$  $10^{3}$

$d$

$3.0$  $3.2$  $3.4$  $3.6$  $3.8$  $4.0$

$600$  $650$  $700$  $750$  $800$  $850$  $900$  $950$

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Outlook

Study on the firing environment: oxidizing and reducing

Better define the mesoscopic structures

*Sampling of a wider geographical area*

Other typologies of materials
On the Adriatic coast of the south of Italy, the “Cantiere Mitello”, close to Otranto in the Apulian region of Salento, is one of the few Mediterranean production centres which can be attributed to the early Middle Ages.

In the site two kind of artefacts can be recognized: the transport amphorae and a series of objects such as pots, saucepans, basins, lids and small pitchers which belong to the domestic life.