Advanced X-ray protocol for the technological study of archaeological ceramics

European Conference on X-Ray Spectrometry 2026

EXRS 2026 EUROPEAN CONFERENCE ON X-RAY SPECTROMETRY

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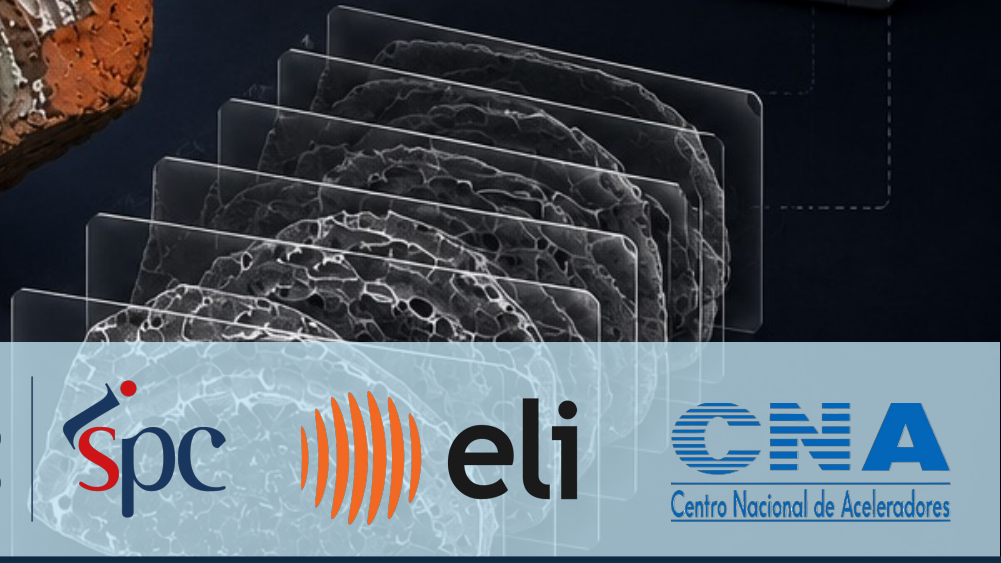

POLITECNICO MILANO 1863 · NanoLab · RAYLAB spin off POLITECNICO DI MILANO · SPC · eli · CNA Centro Nacional de Aceleradores

Archaeological questions for ceramic objects

How can we characterise Roman age glazing technology?

Which was the technological use of the ceramic artifacts?

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Problem to address:

Stratigraphy in glazings

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Diffusion of compounds in bulk

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Case study 1

Glazed ceramic lamp fragment (III A.C) from excavation in Milan

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Ceramic pot fragments (III-I B.C) from excavation in Milan

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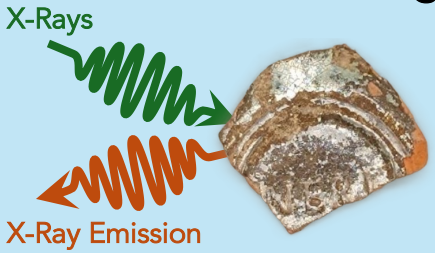
Need for non-invasive characterisation of subsurface structure

Multi-technique approach

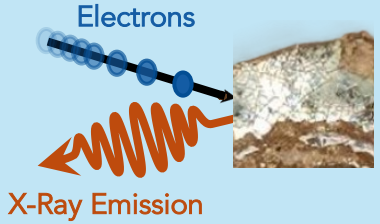
Elemental mapping and imaging

Micro-XRF scanning



Macroscopic elemental mapping

SEM-EDX



Sub-µm features

Micro computer tomography (CT)

Density-sensitive 3D reconstruction

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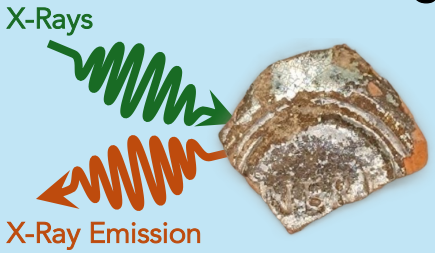

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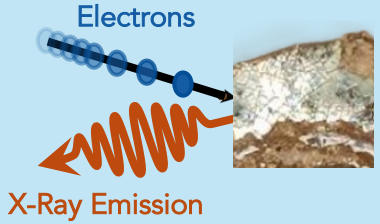

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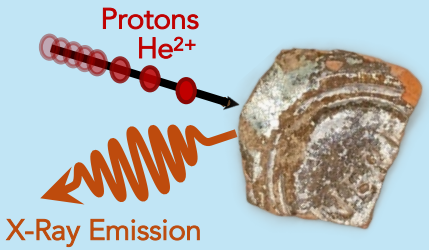
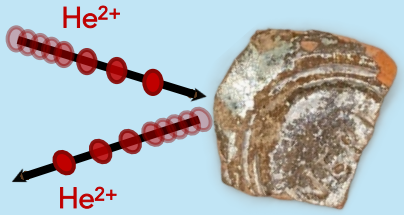
Depth-sensitive elemental and molecular composition analysis

PIXE and differential PIXE



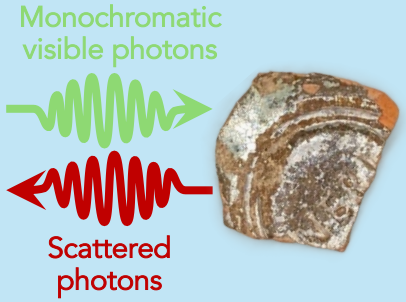
Elemental composition, elemental depth-distribution (10s of µm)

Rutherford backscattering (RBS)



Elemental composition, elemental depth-distribution (10s of nm)

Raman spectroscopy



Molecular composition

Multi-technique approach

Elemental mapping and imaging

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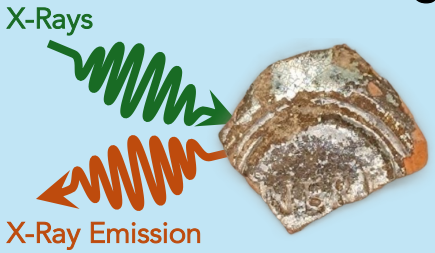

Macroscopic elemental mapping

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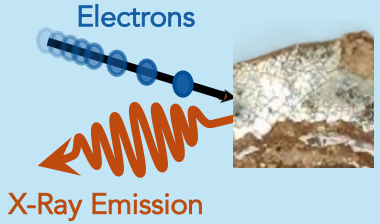

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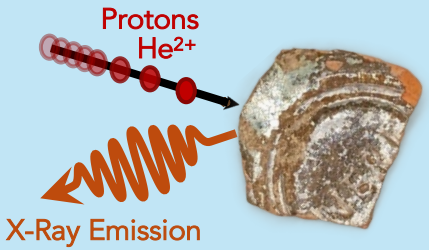

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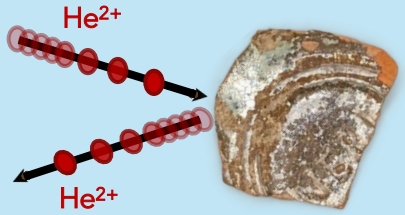

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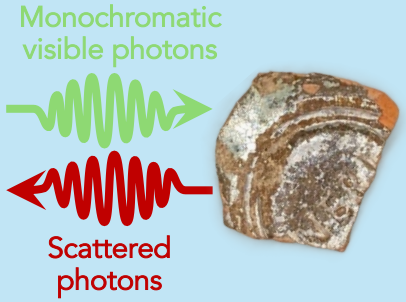
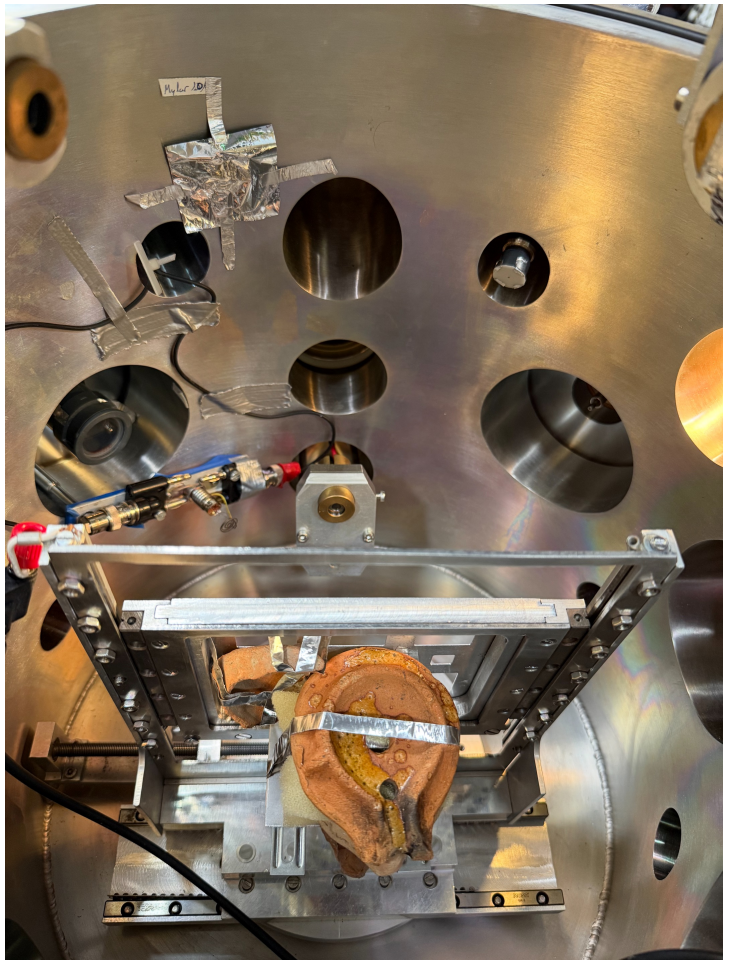
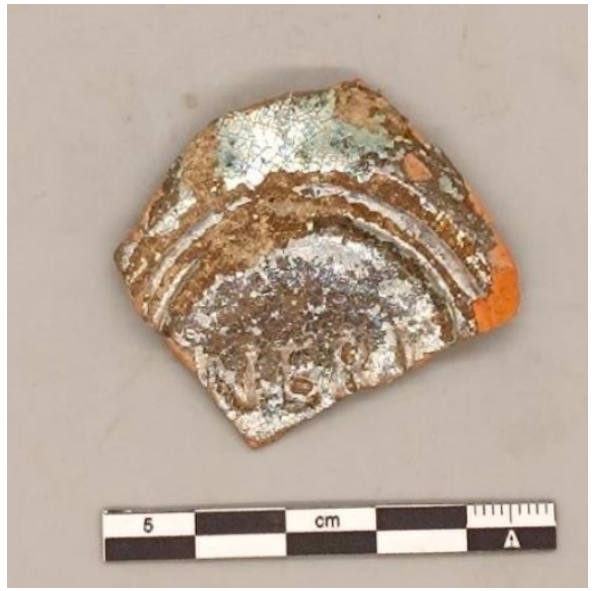


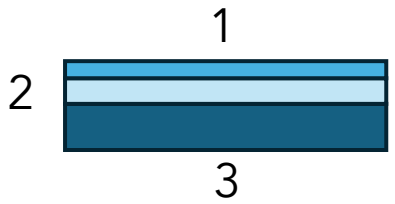
Molecular composition



Setup for PIXE in vacuum @ Centro Nacional de Aceleradores

Glazed oil lamp fragment

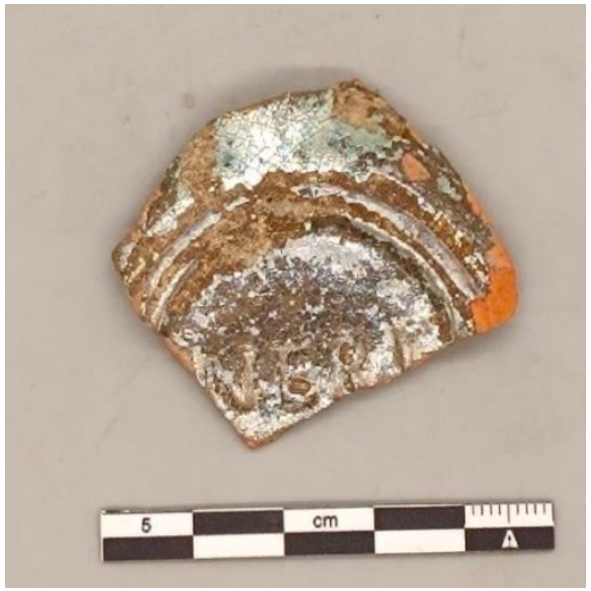


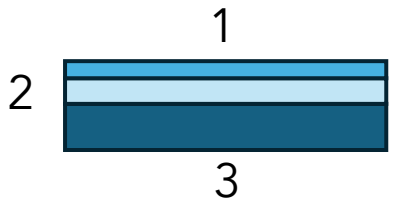


Hypothesis of structure

1. Metal-bearing layer (100s of μm)
2. Glass layer (100s of μm)
3. Ceramic bulk

Glazed oil lamp fragment





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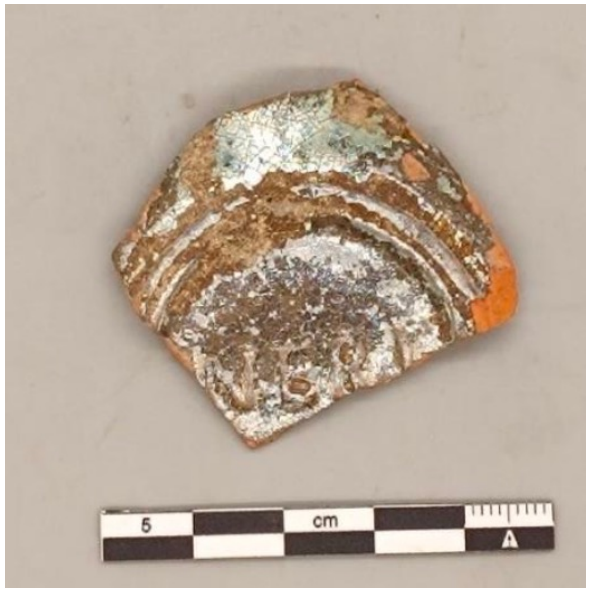
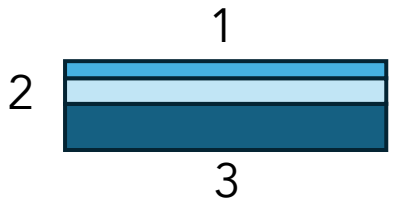
How can we characterise Roman age glazing technology?

Glazed oil lamp fragment





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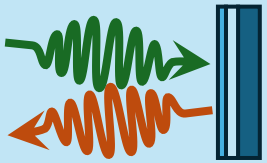
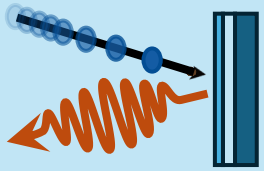
How can we characterise Roman age glazing technology?

1. Micro-XRF



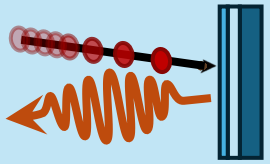
Which elements are present? How are they distributed?

2. SEM-EDX



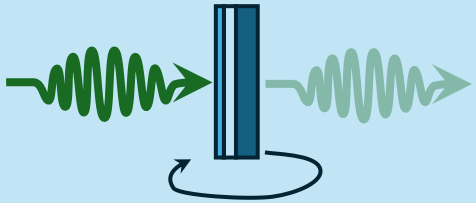
Is there any sub-μm feature in elemental distribution?

3. Differential PIXE



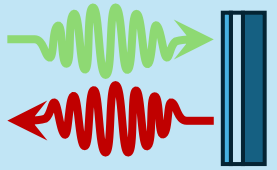
Which is the stratigraphic distribution of the mapped elements?

4. Micro-CT



Which is the thickness of the layers?

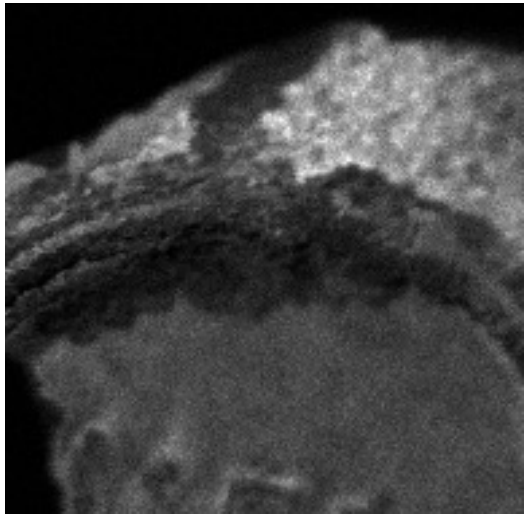
5. Micro-Raman



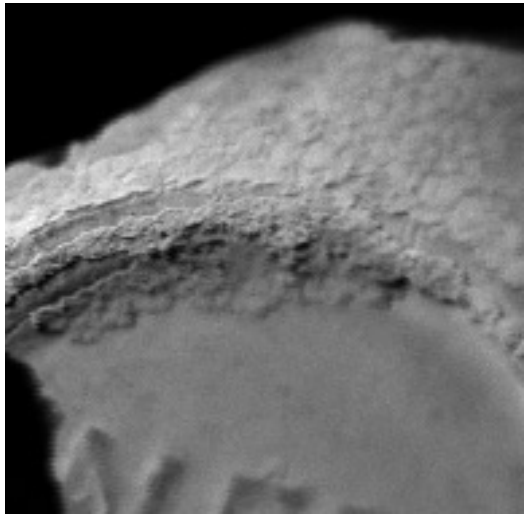
Is there any opacifier, colorant or degradation product?

Glazed oil lamp fragment – micro-XRF

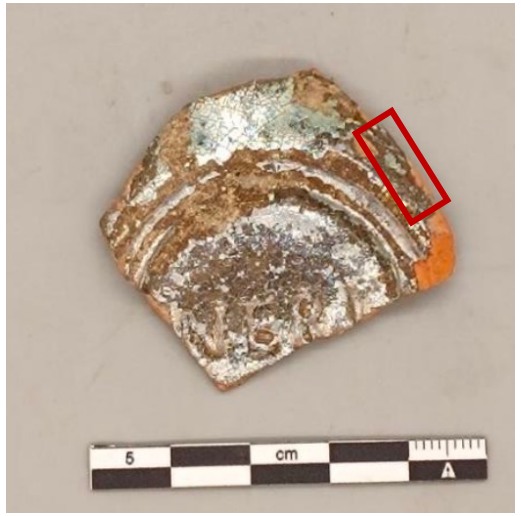
Cu – Kα

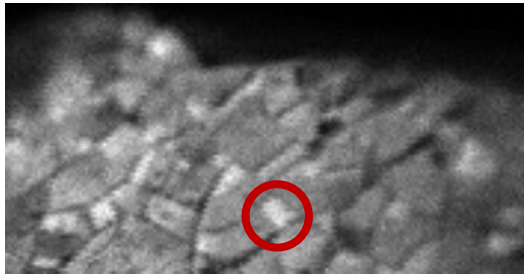


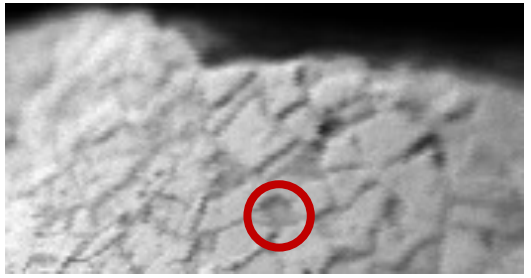
Pb – Lα



In-air micro-XRF scanning @ - X-Ray Lab (Catania)







F.P. Romano *et al.*, *Anal. Chem.*, *88:22* (2016)

Glazed oil lamp fragment – micro-XRF

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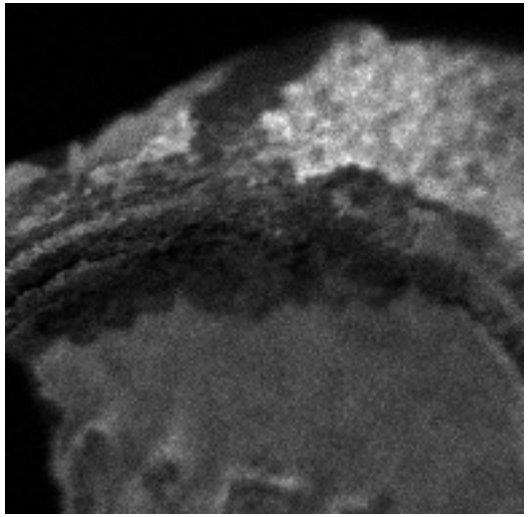
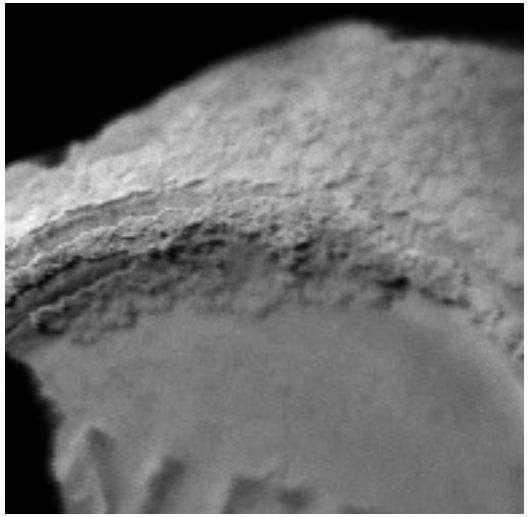
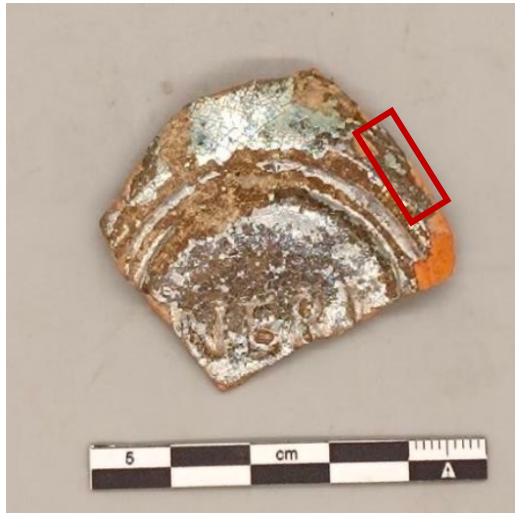


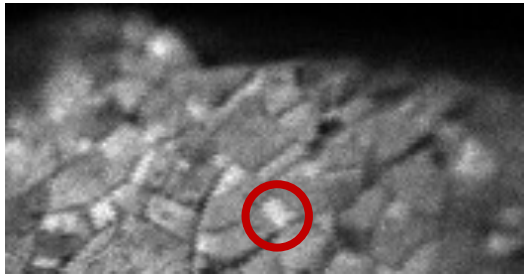
Pb – Lα

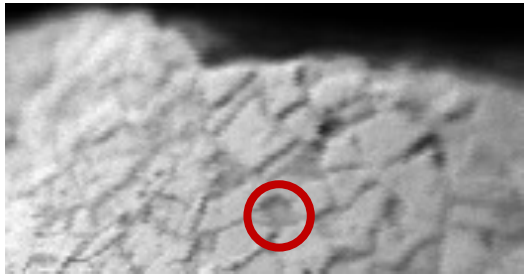


In-air micro-XRF scanning @ | - X-Ray Lab (Catania)

Cu present where glass is intact







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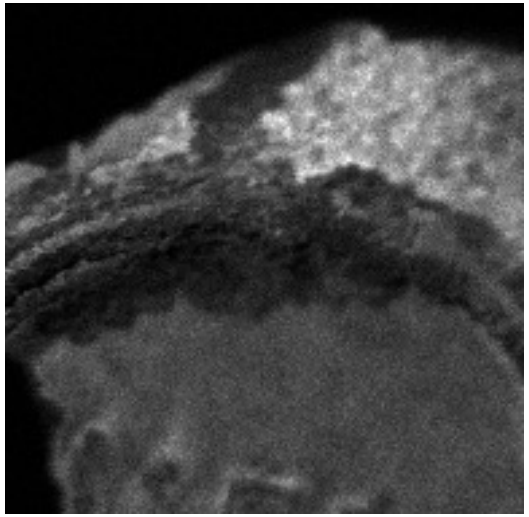
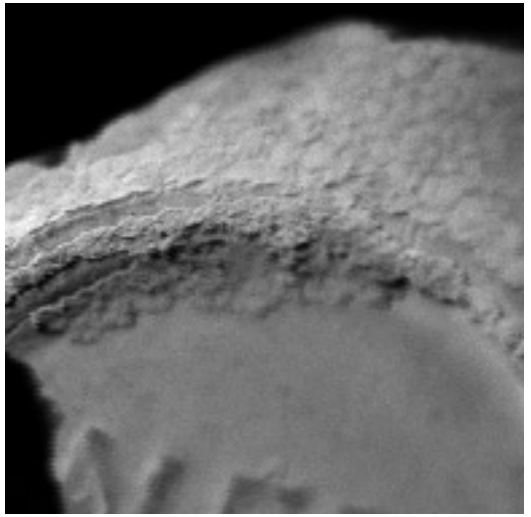
Glazed oil lamp fragment – micro-XRF

Cu – Kα



Pb – Lα



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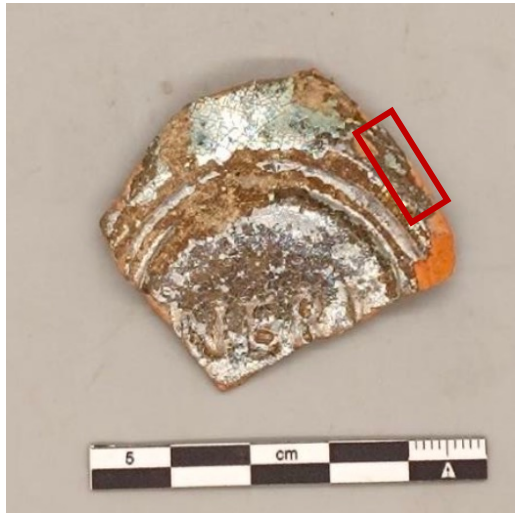
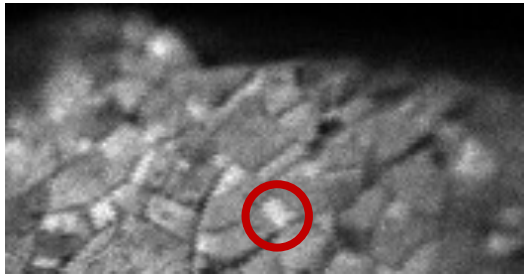
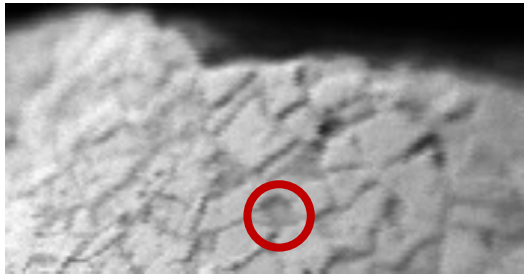
Cu present where glass is intact





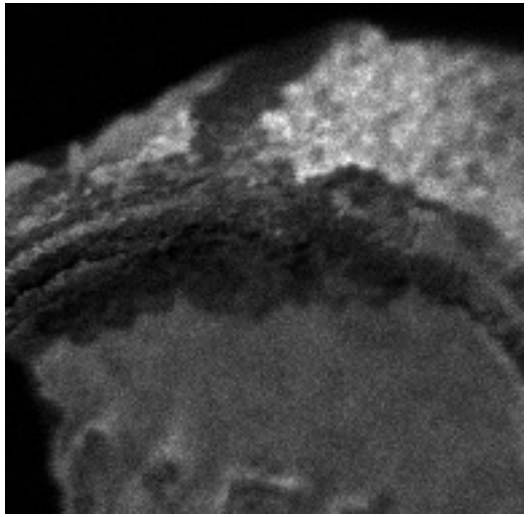


Anticorrelation between **Cu** and **Pb**

F.P. Romano *et al.*, *Anal. Chem.*, *88:22* (2016)

Glazed oil lamp fragment – micro-XRF

Cu – Kα



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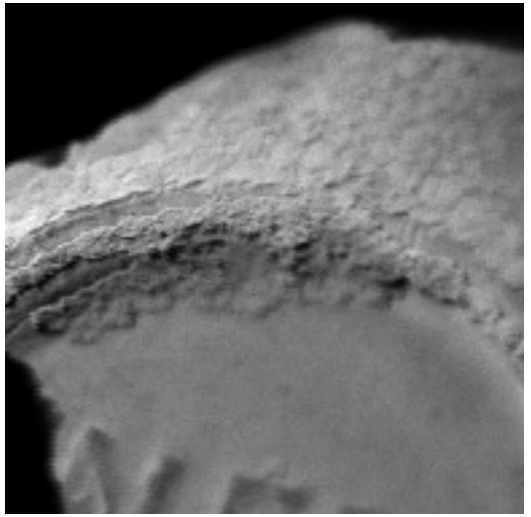

In-air micro-XRF scanning @ | spc
- X-Ray Lab (Catania)

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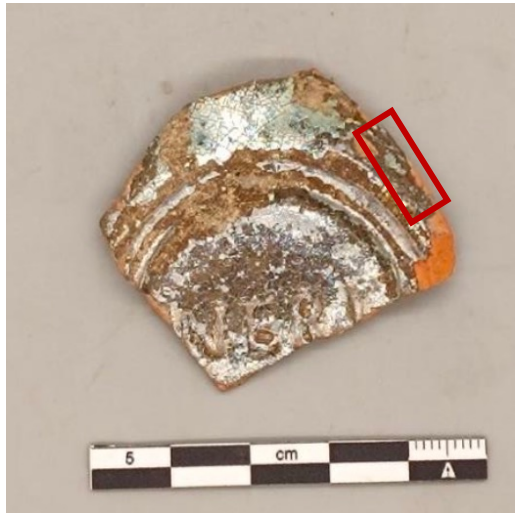
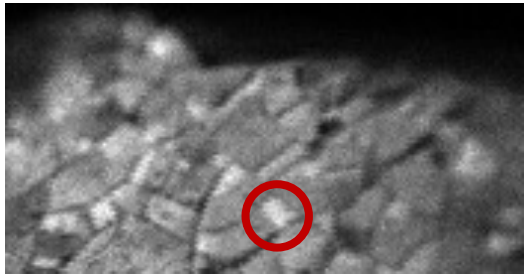
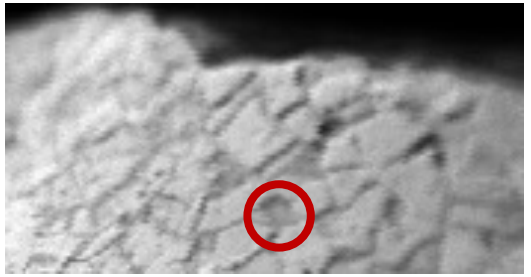




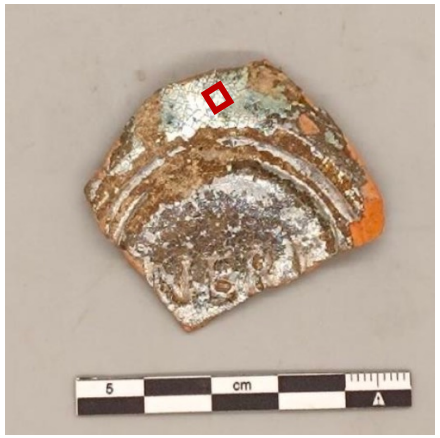


Anticorrelation between **Cu** and **Pb**

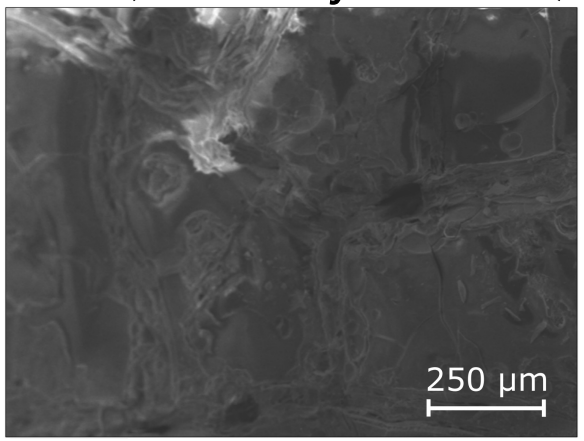
Is Cu a chromophore?
Is Cu on surface?

F.P. Romano *et al.*, *Anal. Chem.*, *88:22* (2016)

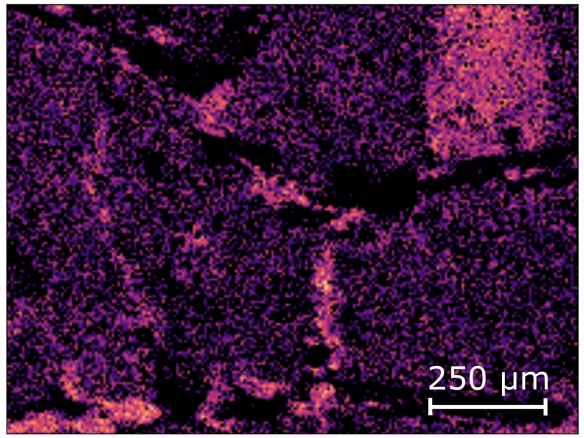
Glazed oil lamp fragment – SEM-EDX

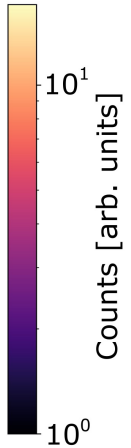


SEM (secondary electrons)

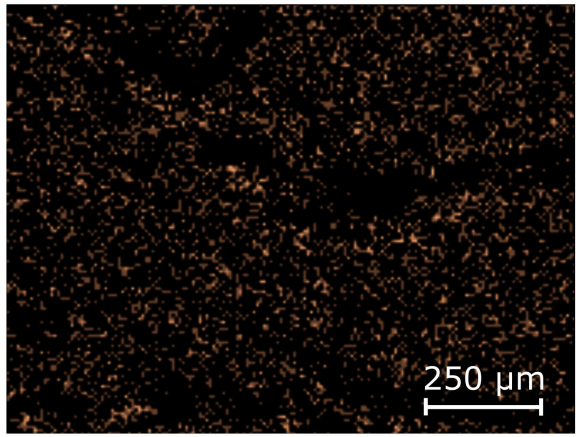


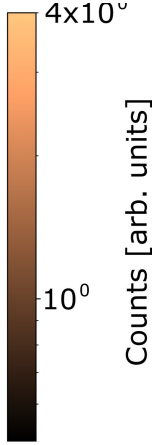
Pb – Mα





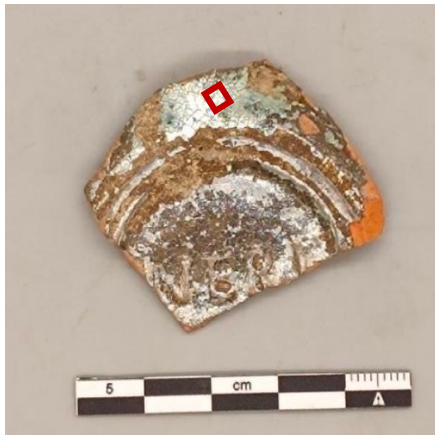
Cu – Lα



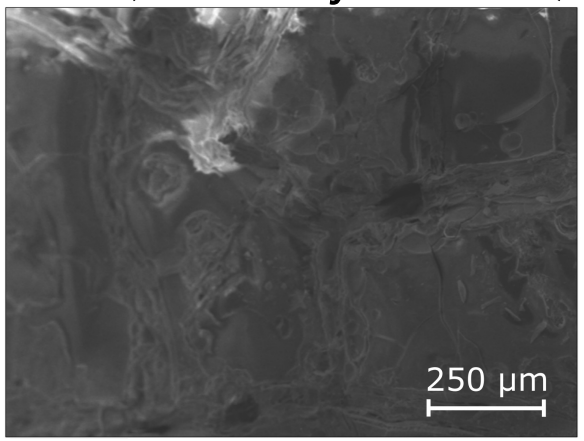


SEM-EDX performed @ NanoLab with a Zeiss Supra 40 field-emission SEM coupled with EDX on whole object

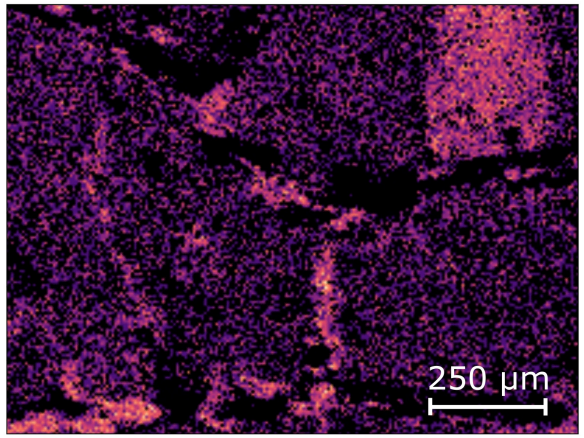
Glazed oil lamp fragment – SEM-EDX

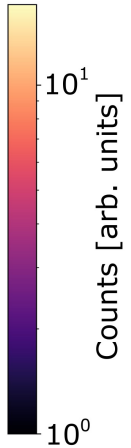


SEM (secondary electrons)

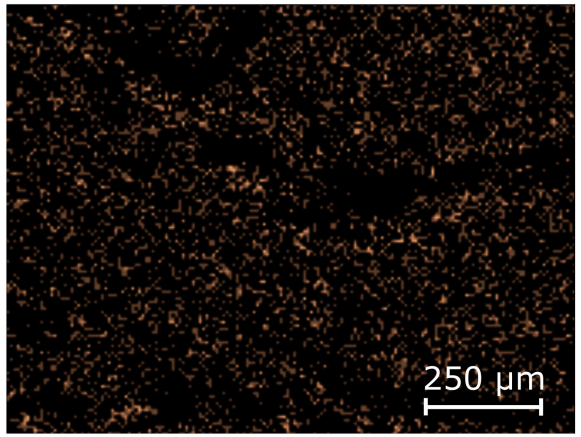


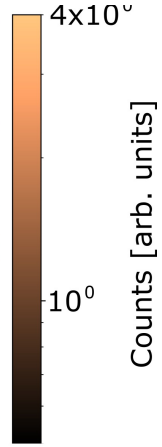
Pb – Mα





Cu – Lα

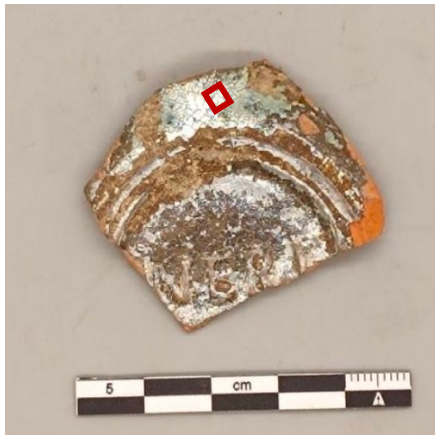




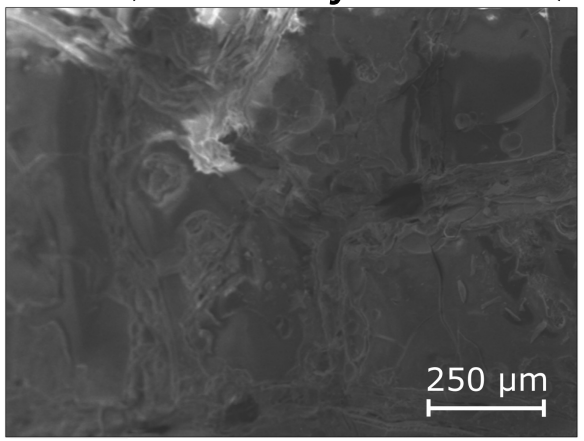
SEM-EDX performed @ NanoLab with a Zeiss Supra 40 field-emission SEM coupled with EDX on whole object

Pb and **Cu** present in the surface (low energy lines)

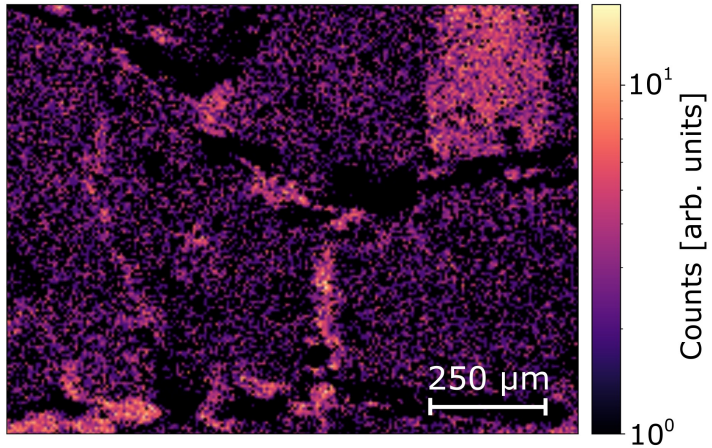
Glazed oil lamp fragment – SEM-EDX



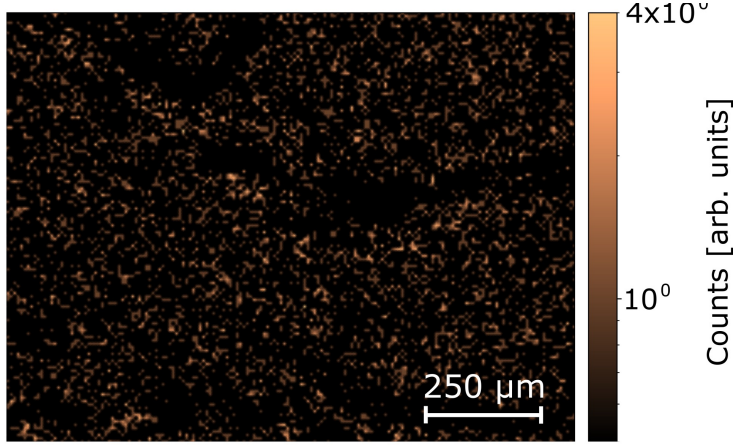
SEM (secondary electrons)



Pb – Mα



Cu – Lα



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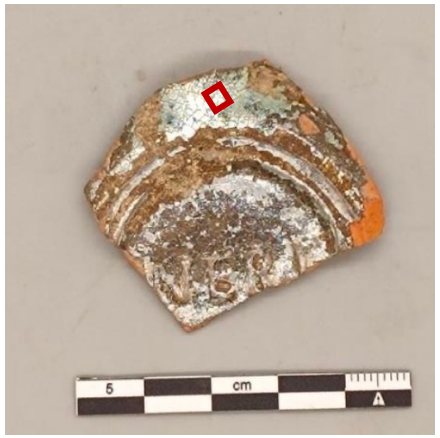
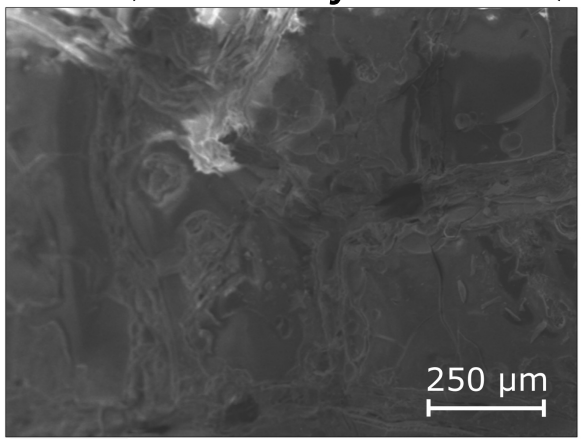
Pb and **Cu** present in the surface (low energy lines)

Pb more intense on fractures

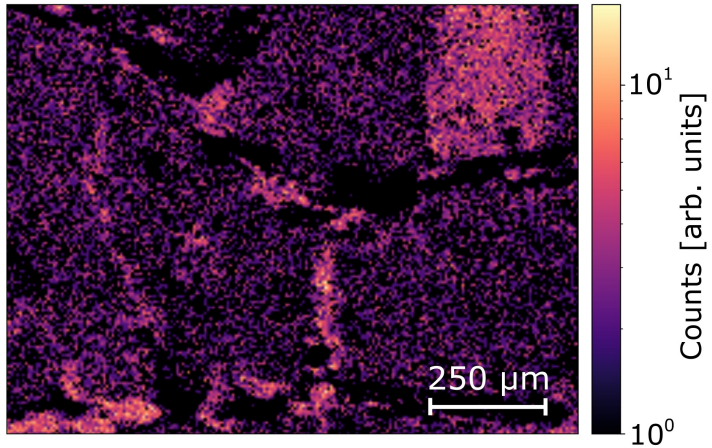
Glazed oil lamp fragment – SEM-EDX



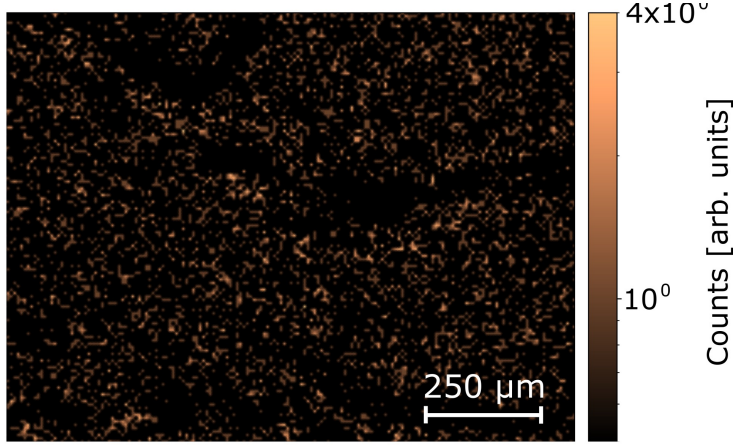
SEM (secondary electrons)



Pb – Mα



Cu – Lα



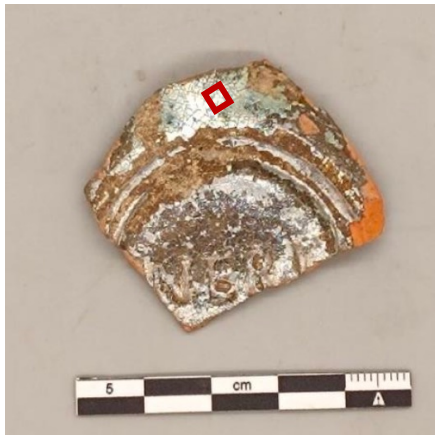
SEM-EDX performed @ NanoLab with a Zeiss Supra 40 field-emission SEM coupled with EDX on whole object

Pb and **Cu** present in the surface (low energy lines)

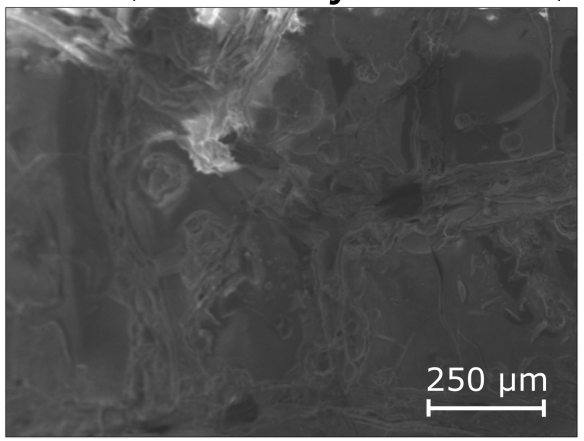
Pb more intense on fractures

Cu less homogeneous than Pb

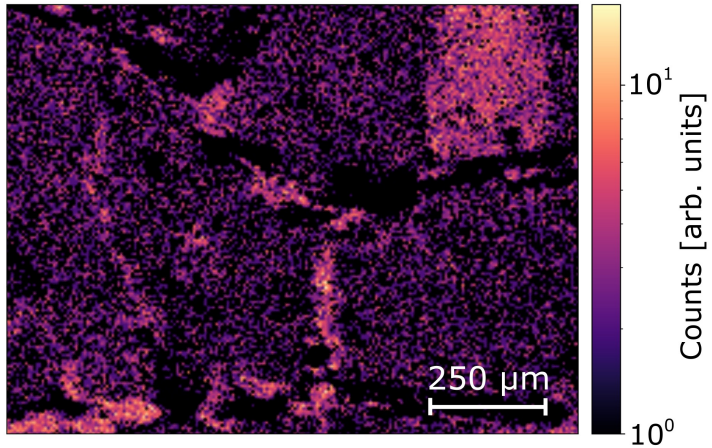
Glazed oil lamp fragment – SEM-EDX



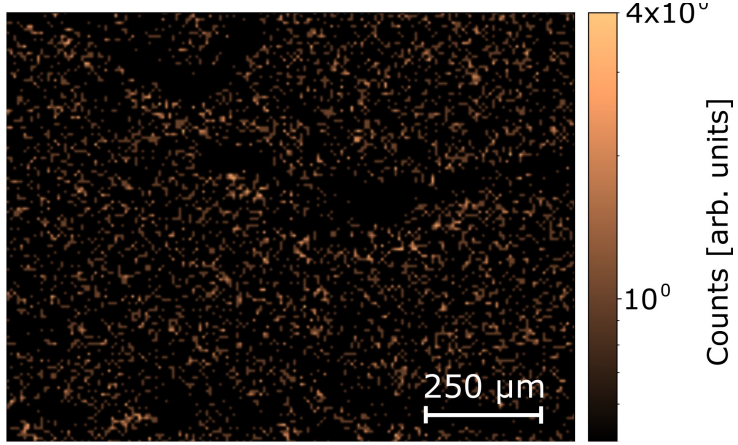
SEM (secondary electrons)



Pb – Ma



Cu – La



SEM-EDX performed @ NanoLab with a Zeiss Supra 40 field-emission SEM coupled with EDX on whole object

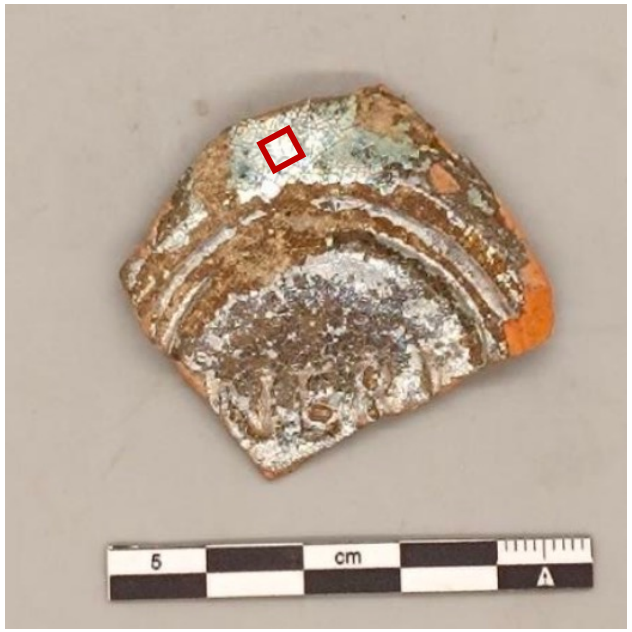
Pb and **Cu** present in the surface (low energy lines)

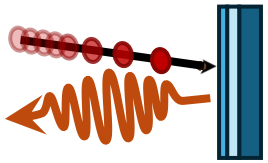
Pb more intense on fractures

Cu less homogeneous than Pb

Resolution limited by sample charging, cannot detect nanoparticle presence

Glazed oil lamp fragment – differential PIXE





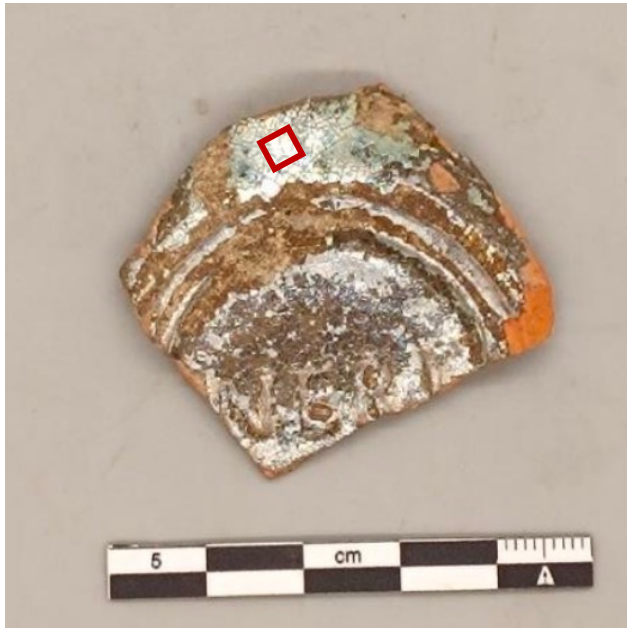
Irradiation of object in vacuum @ CNA Centro Nacional de Aceleradores with:

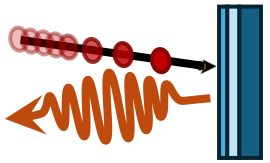
Alphas 3 MeV	Protons 2 MeV	Protons 3 MeV	Protons 4.5 MeV

Increasing particle range

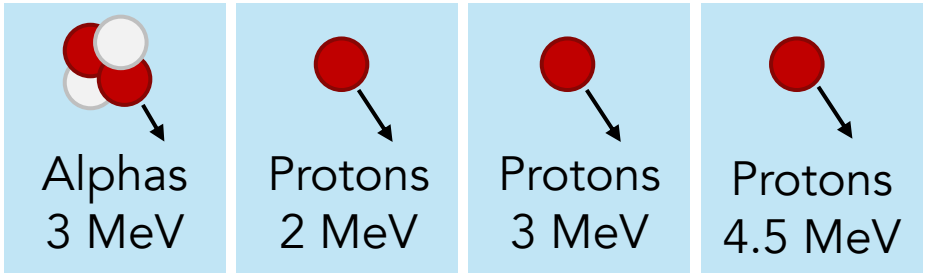
M.A. Respaldiza *et al.*, *Nucl. Instrum. Methods Phys. Res. B, 266:10* (2008)

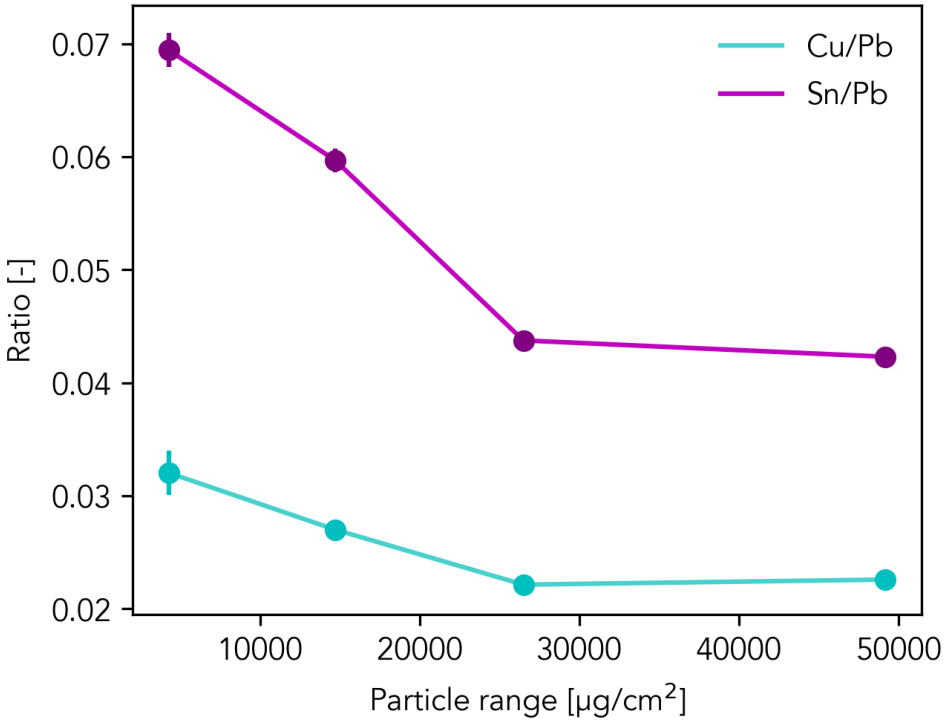
Glazed oil lamp fragment – differential PIXE





Irradiation of object in vacuum @ CNA Centro Nacional de Aceleradores with:



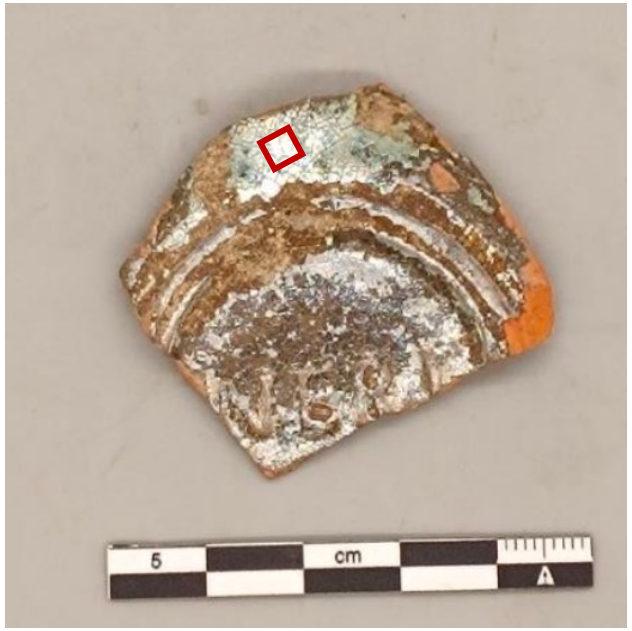


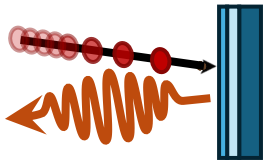
PIXE spectrum analysis with GUPIX considering the material as homogeneous:

Estimated **Cu** and **Sn** over **Pb** concentration **decreasing** with particle range

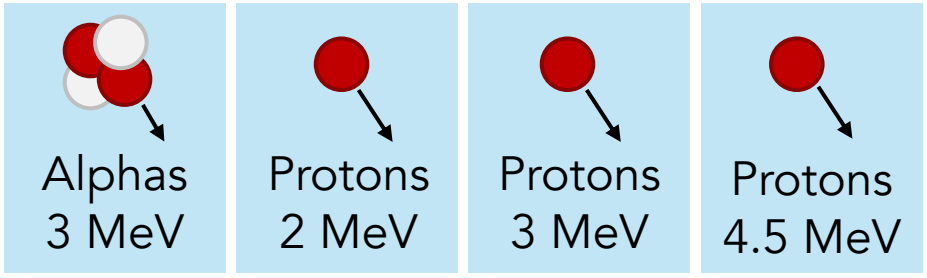
M.A. Respaldiza *et al.*, *Nucl. Instrum. Methods Phys. Res. B, 266:10* (2008)

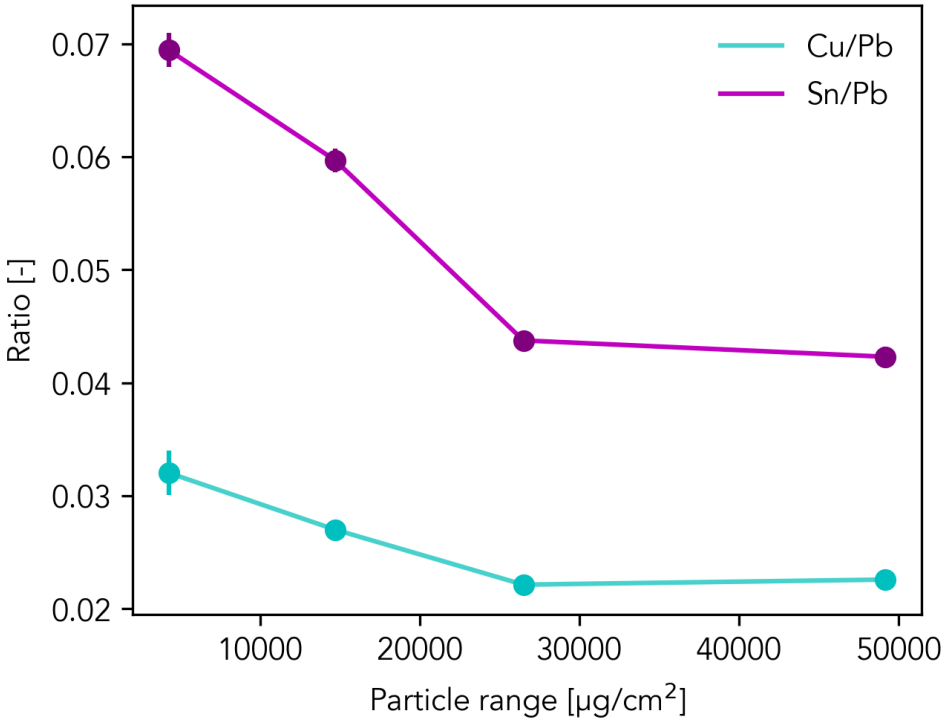
Glazed oil lamp fragment – differential PIXE





Irradiation of object in vacuum @ CNA Centro Nacional de Aceleradores with:





PIXE spectrum analysis with GUPIX considering the material as homogeneous:

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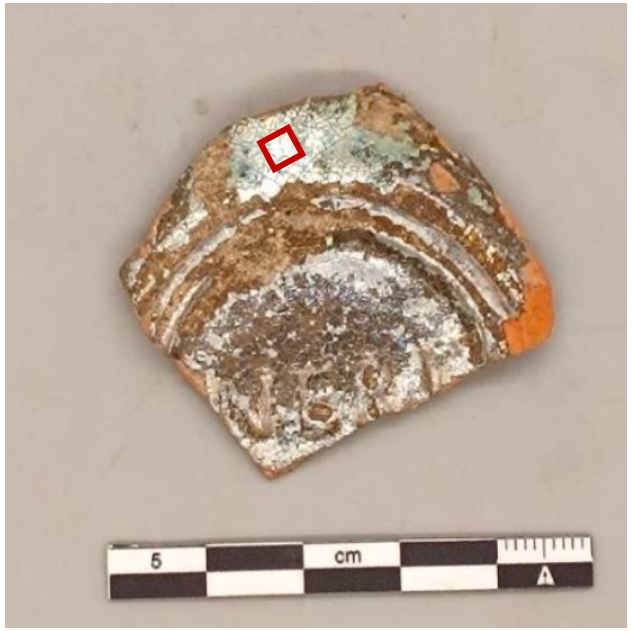
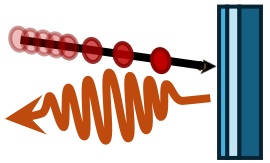
Presence of Cu and Sn on top of the **lead containing surface**

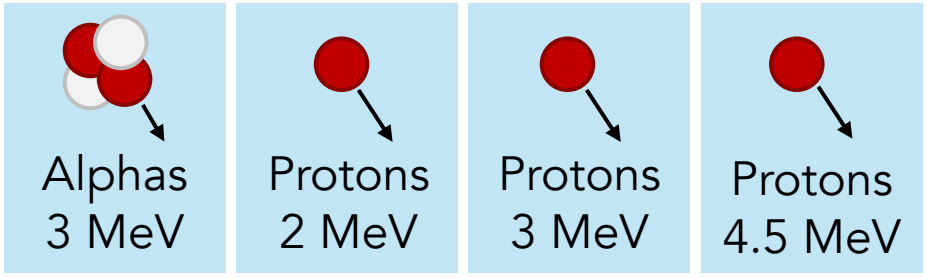
M.A. Respaldiza *et al.*, *Nucl. Instrum. Methods Phys. Res. B, 266:10* (2008)

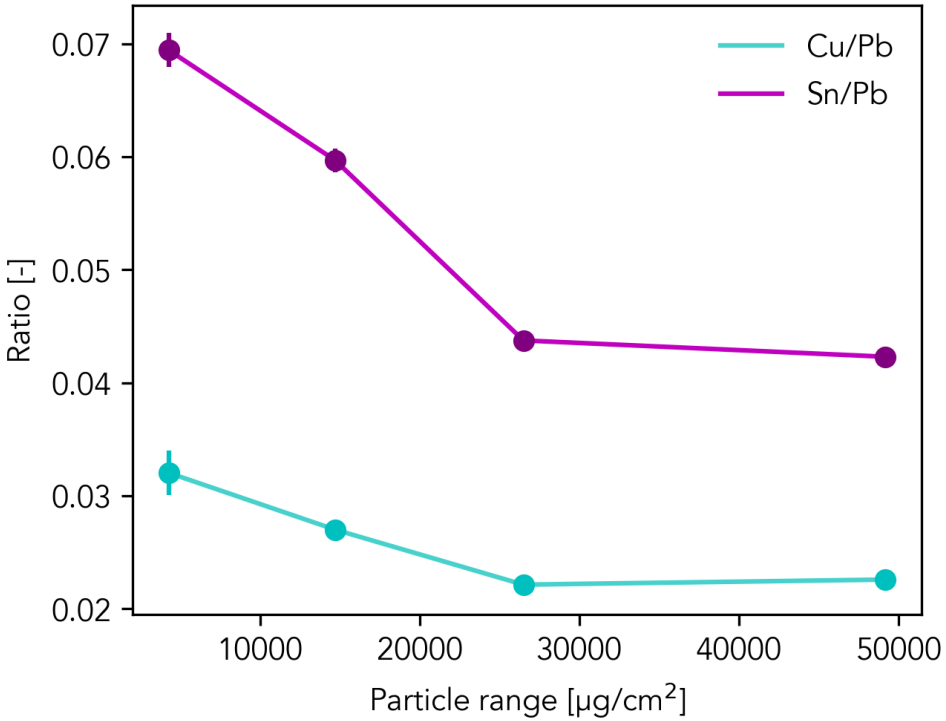
Glazed oil lamp fragment – differential PIXE





Irradiation of object in vacuum @ CNA Centro Nacional de Aceleradores with:





PIXE spectrum analysis with GUPIX considering the material as homogeneous:

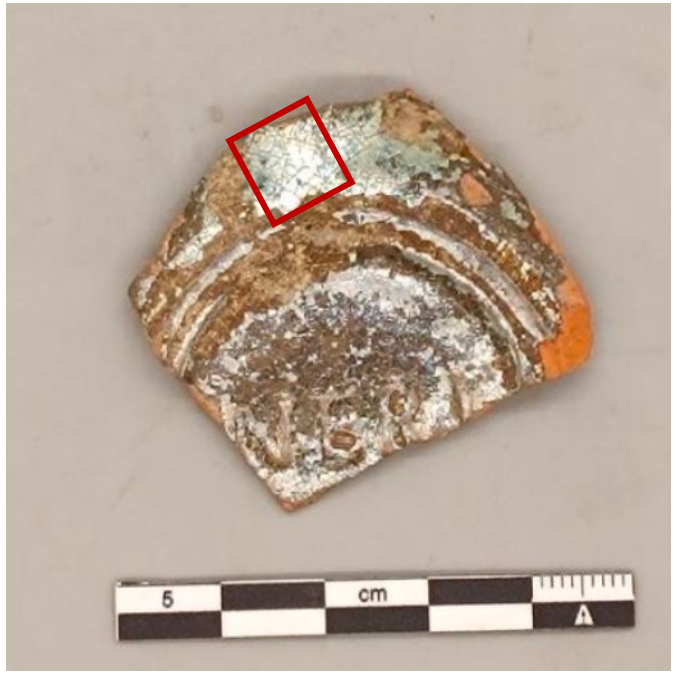
Estimated **Cu** and **Sn** over **Pb** concentration **decreasing** with particle range

Presence of Cu and Sn on top of the **lead containing surface**

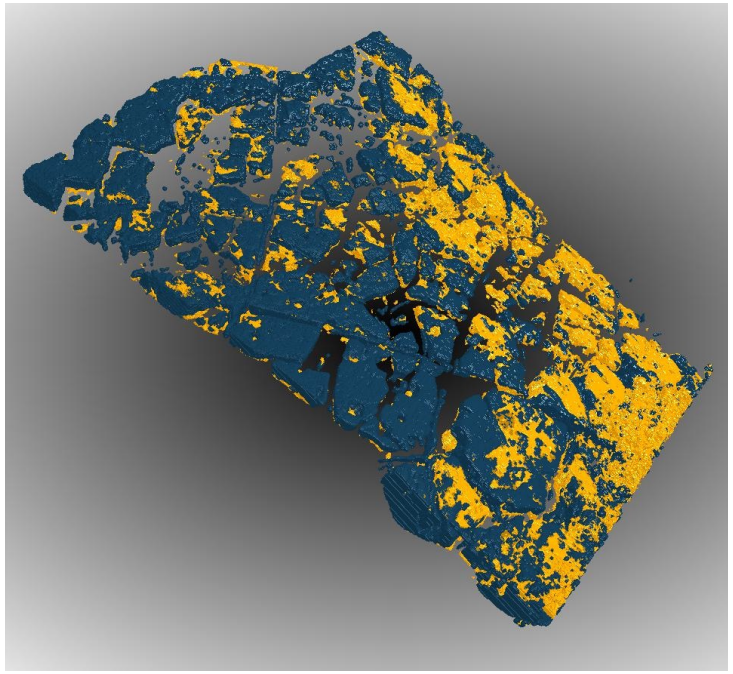
How thick is the metal layer?
Are we analysing glass only?

M.A. Respaldiza *et al.*, *Nucl. Instrum. Methods Phys. Res. B, 266:10* (2008)

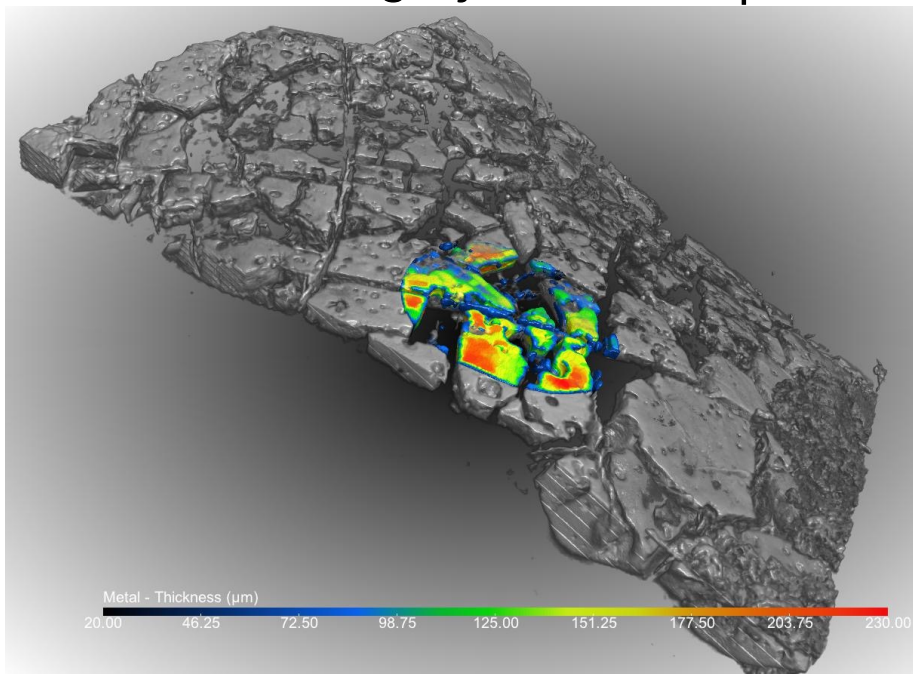
Glazed oil lamp fragment – micro-CT



Phase reconstruction of glass

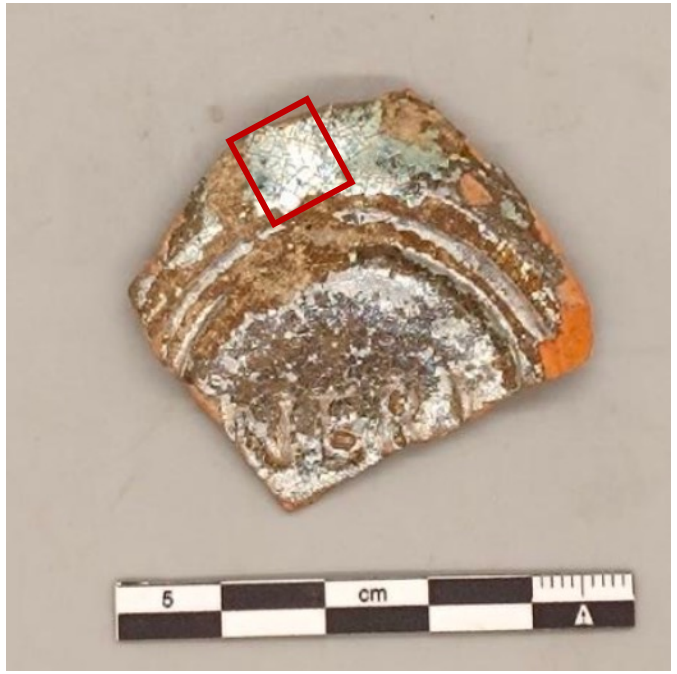


Metal-bearing layer thickness plot



X-ray micro-CT performed @ POLITECNICO MILANO 1863 with a Tescan UniTOM HR operated at 160 kV with 1-mm-Cu filtering

Glazed oil lamp fragment – micro-CT



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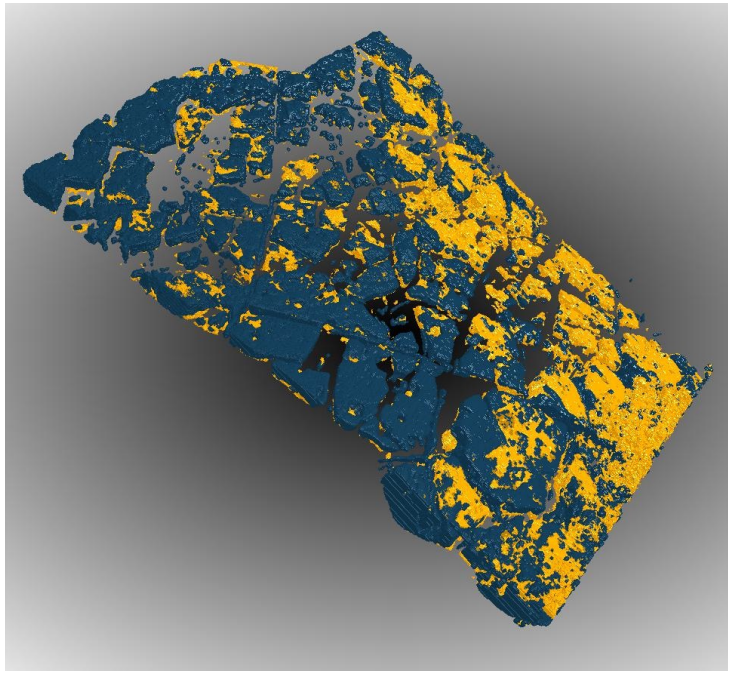

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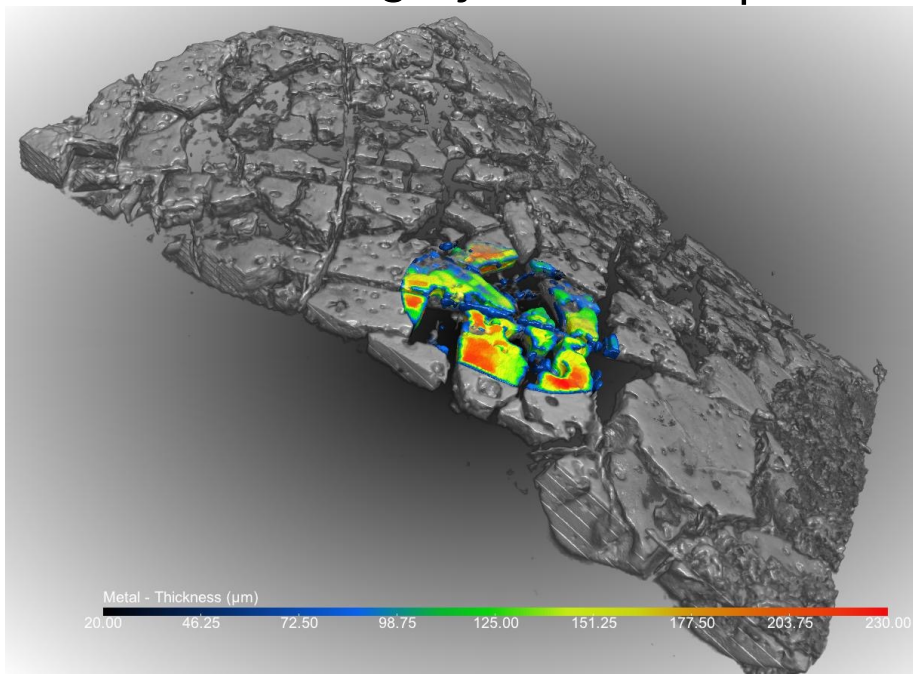
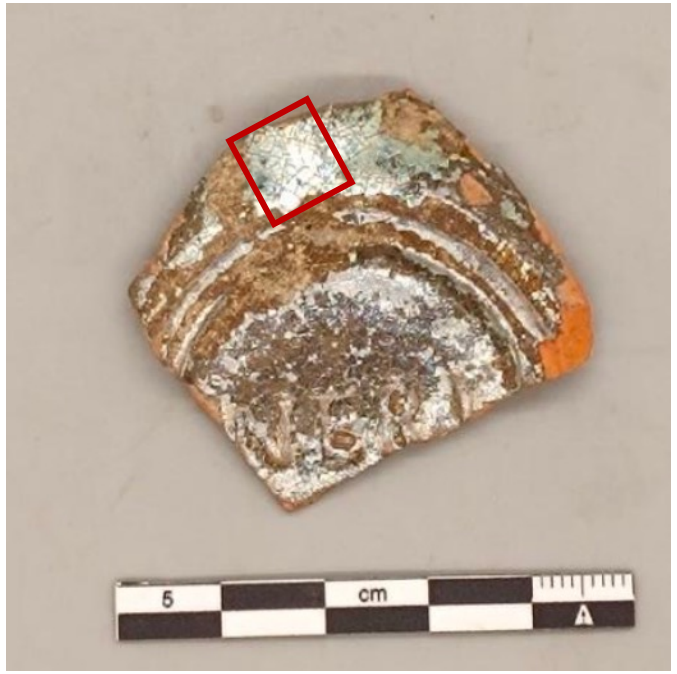


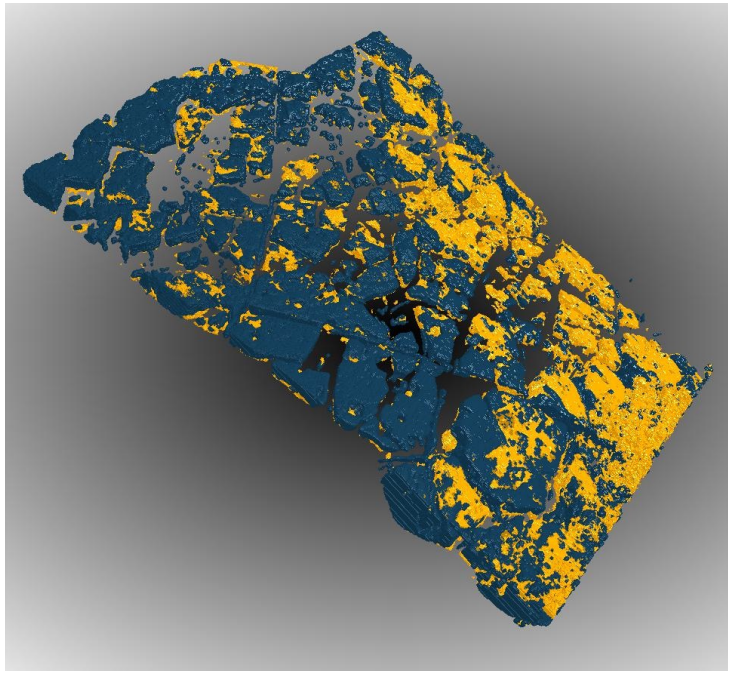
X-ray micro-CT performed @ POLITECNICO MILANO 1863 with a Tescan UniTOM HR operated at 160 kV with 1-mm-Cu filtering

Presence of **2 phases** in glass, relatable to a denser **metal-bearing layer** on **top (blue)**

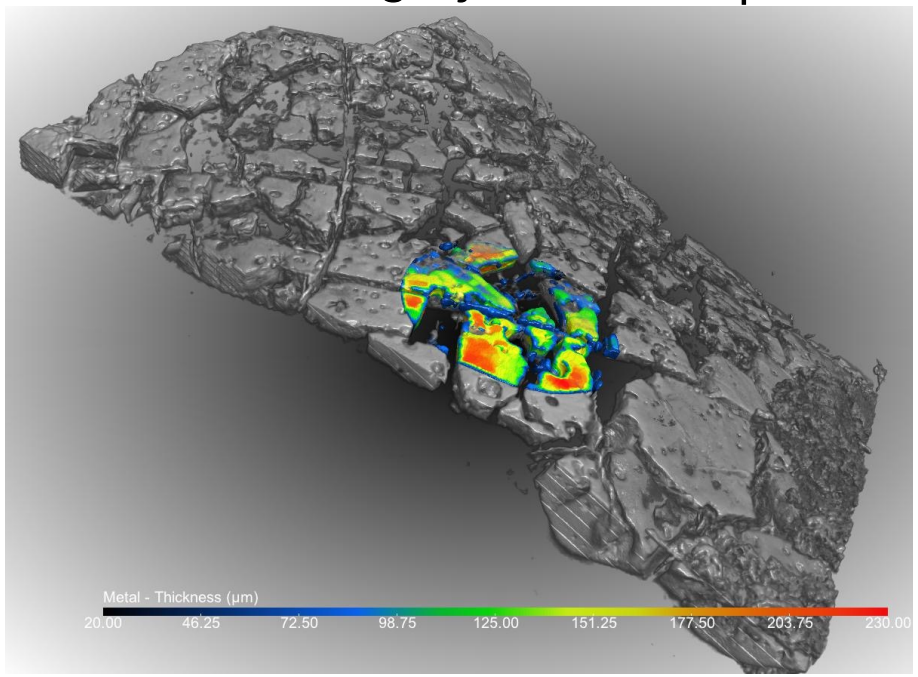
Glazed oil lamp fragment – micro-CT



Phase reconstruction of glass



Metal-bearing layer thickness plot



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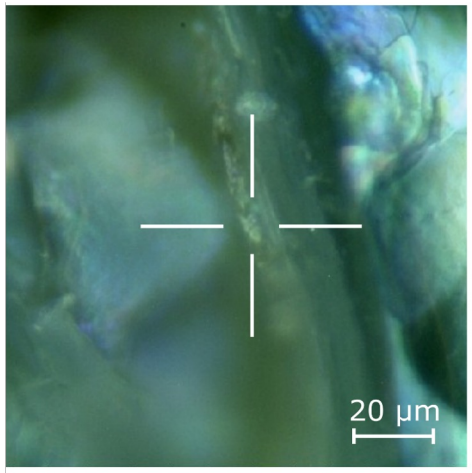
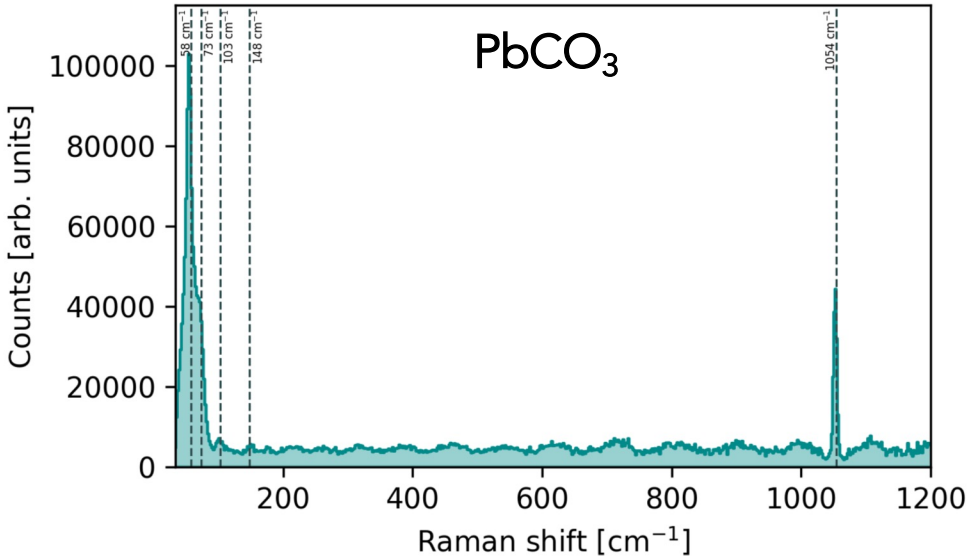
Presence of **2 phases** in glass, relatable to a denser **metal-bearing layer** on **top (blue)**

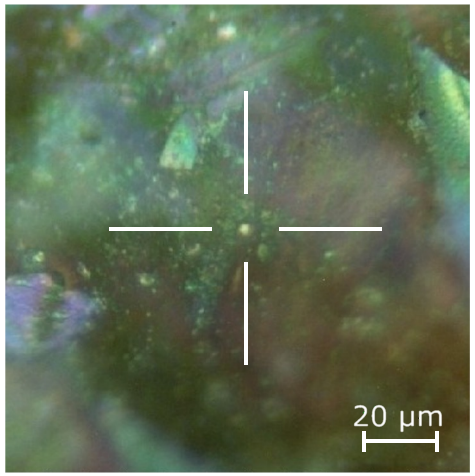
Glass thickness ~200 µm, metal thickness ~100 µm: ions entirely **stopped** in the **glass**

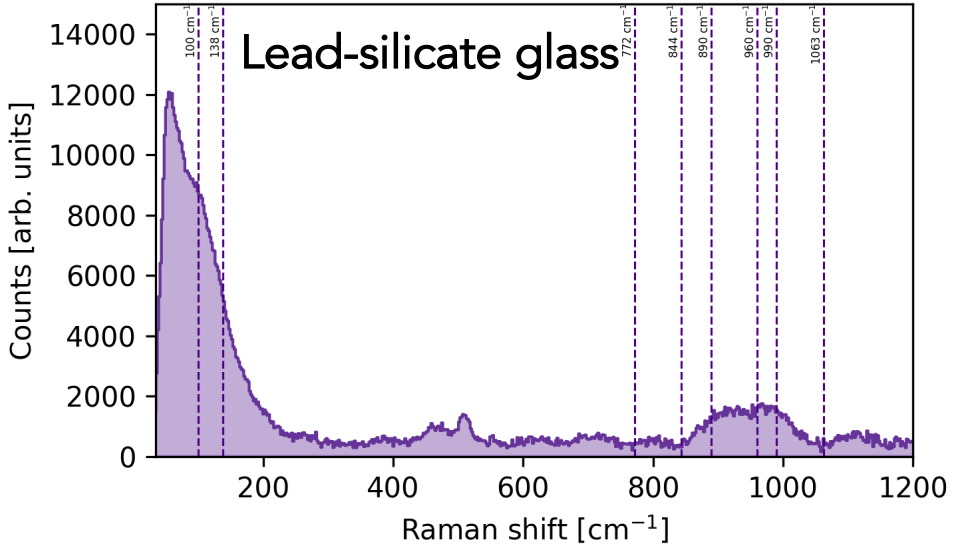
Glazed oil lamp fragment – micro-Raman



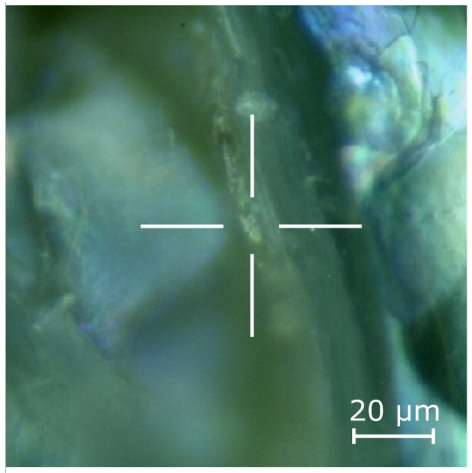


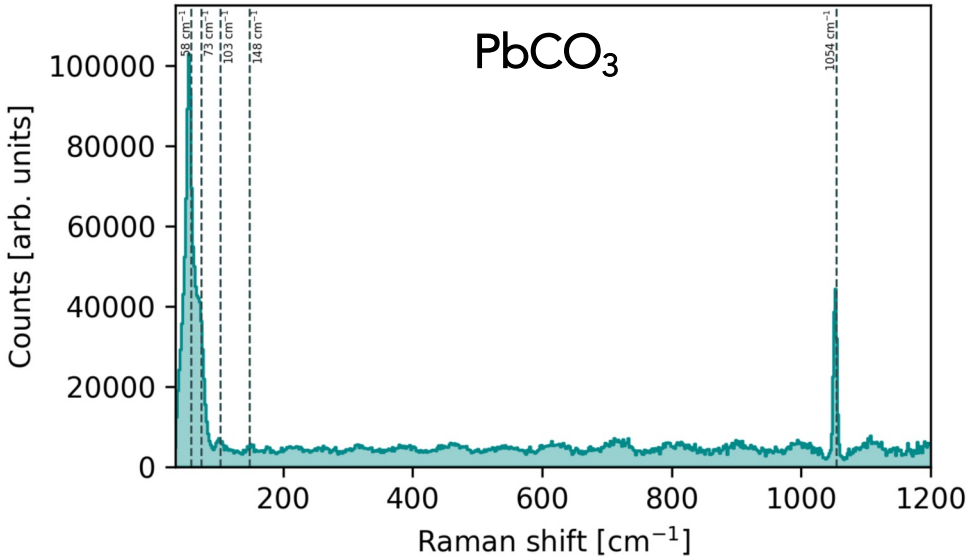
Raman performed @ NanoLab with Renishaw inVia Qontor





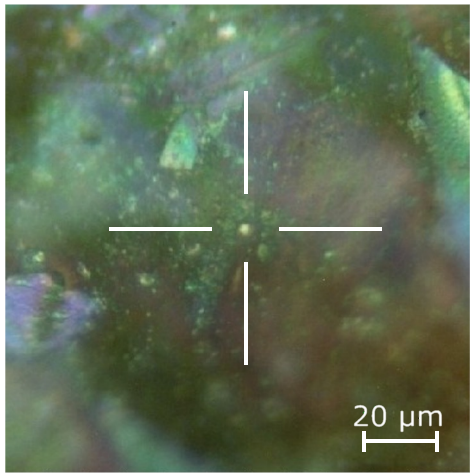
Glazed oil lamp fragment – micro-Raman

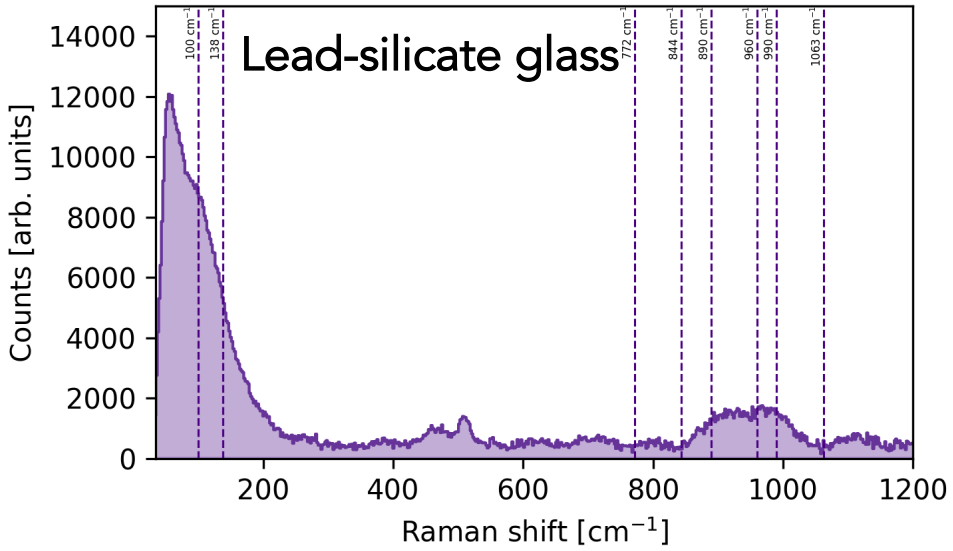




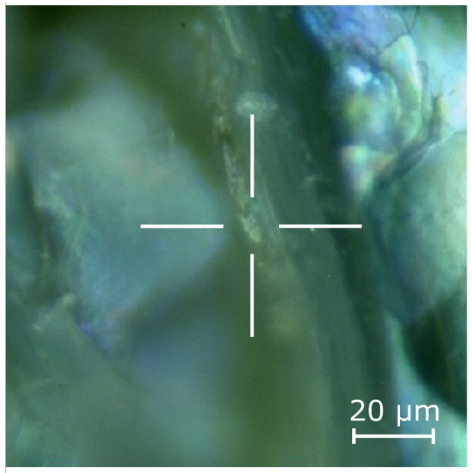
Raman performed @ NanoLab with Renishaw inVia Qontor

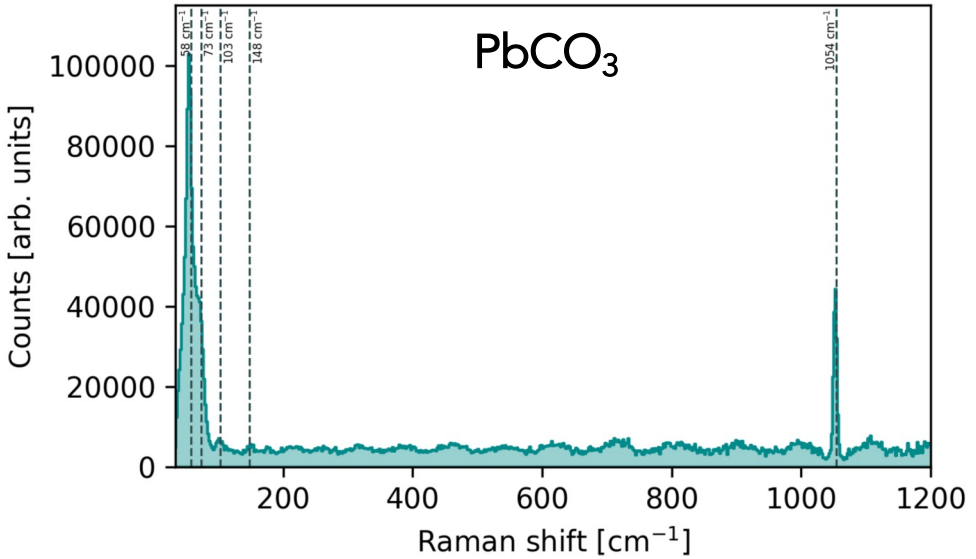
Presence of cerussite relatable to **opacifier** or **degradation** product





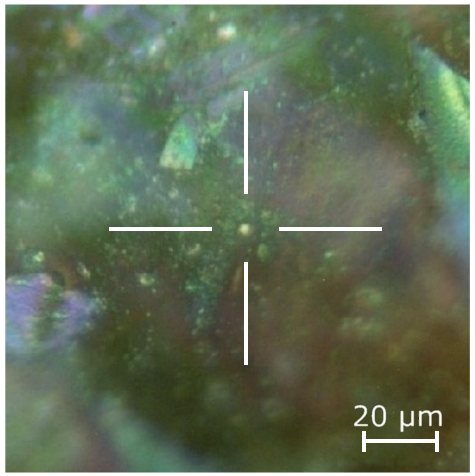
Glazed oil lamp fragment – micro-Raman

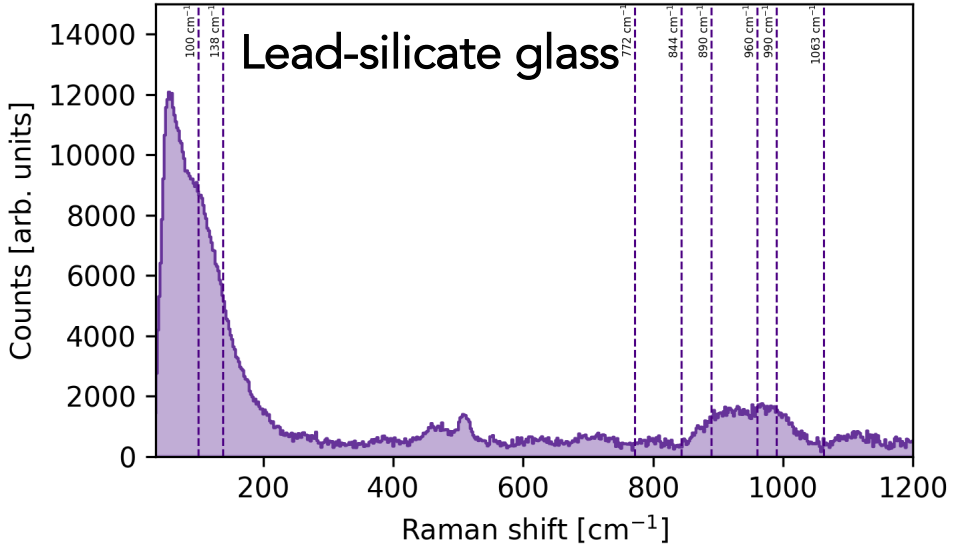




Raman performed @ NanoLab with Renishaw inVia Qontor

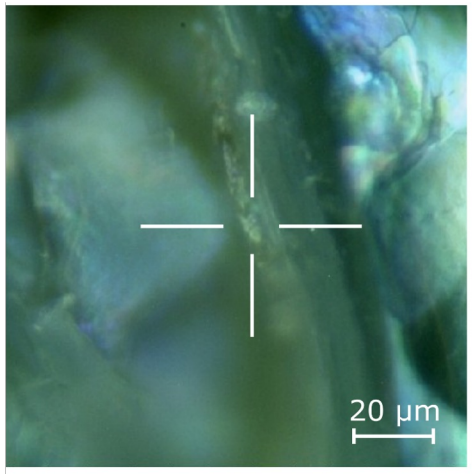
Presence of cerussite relatable to **opacifier** or **degradation** product

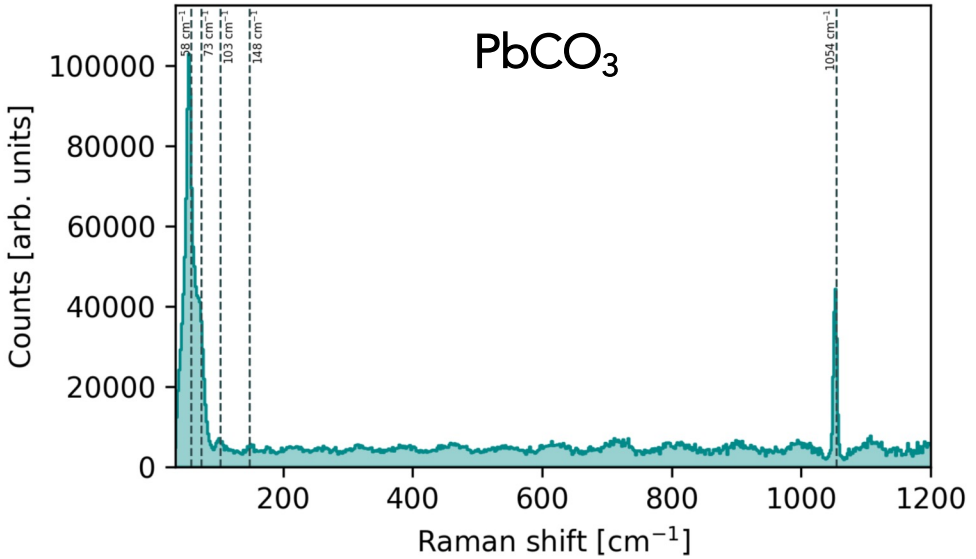




Molecular confirmation of a **lead-silicate glass**

Glazed oil lamp fragment – micro-Raman





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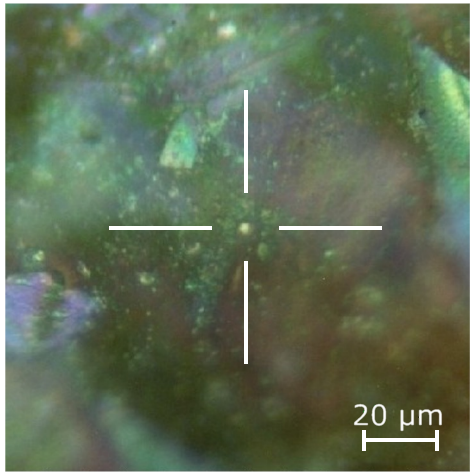

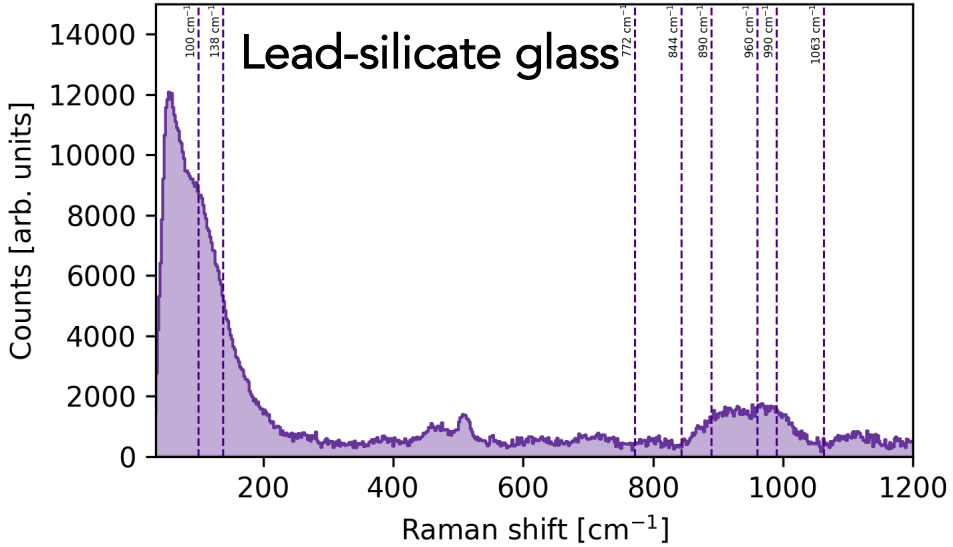

Molecular confirmation of a **lead-silicate glass**

Understand the depth distribution of $PbCO_3$

Glazed oil lamp fragment – Protocol results

Connected results from **elemental composition to 3D imaging** of the artifact

Non-invasively assessed the **layered structure** in the ceramic glazing

Observed molecular traces relatable to possible presence of **opacifiers**

Glazed oil lamp fragment – Protocol results

Connected results from **elemental composition to 3D imaging** of the artifact

Connected to glazing production techniques

Non-invasively assessed the **layered structure** in the ceramic glazing

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Glazed oil lamp fragment – Protocol results

Connected results from **elemental composition to 3D imaging** of the artifact

Connected to glazing production techniques

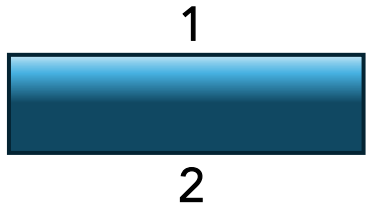
Non-invasively assessed the **layered structure** in the ceramic glazing

Observed molecular traces relatable to possible presence of **opacifiers**

Determine the **copper function** in the glass (e.g., chromophore) through SEM-EDX

Assess whether **cerussite** is opacifier or degradation product through confocal scanning with Raman

Ceramic pot fragments

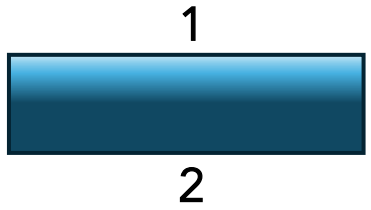


Hypotised structure from preliminary analysis

1. Metal diffusion layer (100s of nm)
2. Ceramic bulk

Ceramic pot fragments

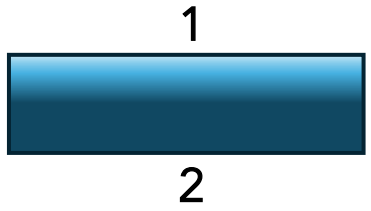
Hypotised structure from preliminary analysis



1. Metal diffusion layer (100s of nm)
2. Ceramic bulk

Which was the technological use of these ceramic artifacts?

Ceramic pot fragments



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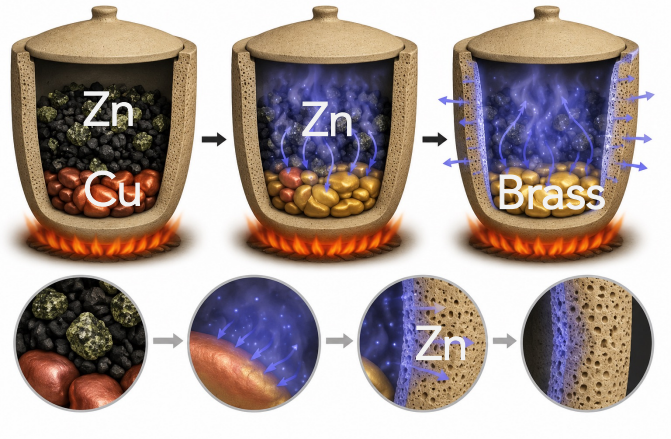

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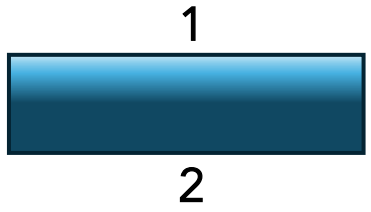
Ceramic pot fragments



Hypotised structure from preliminary analysis

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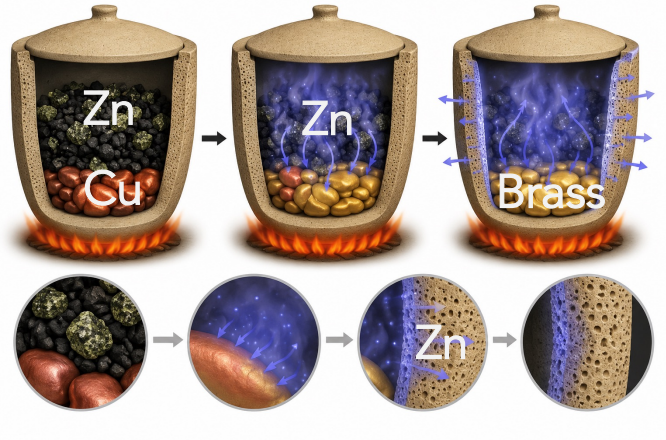
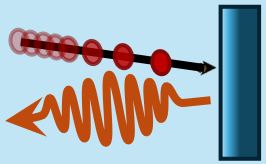
2. Ceramic bulk



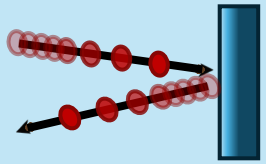
Which was the technological use of these ceramic artifacts?

1. PIXE



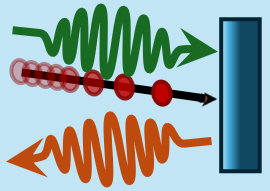
Which elements can be related to technological uses?

2. RBS



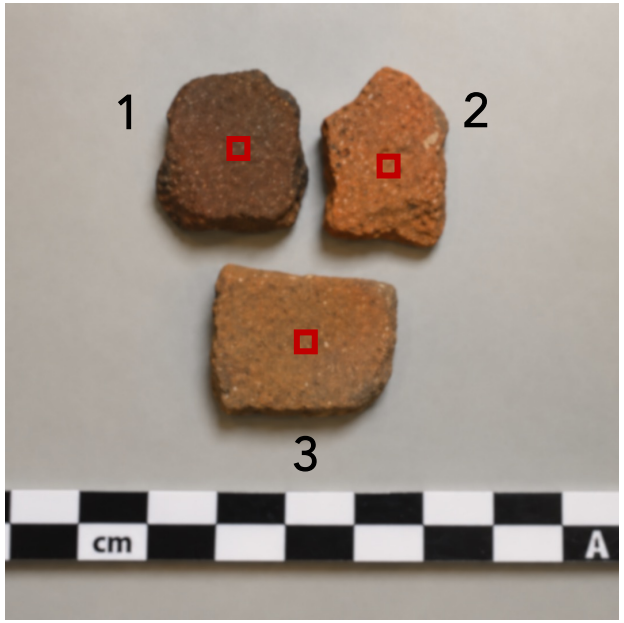
Is there any sub-µm elemental diffusion feature?

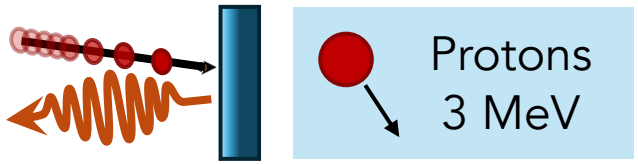
3. Laser-based PIXE



Can we use non-conventional sources for heritage science?

Ceramic pot fragments – PIXE



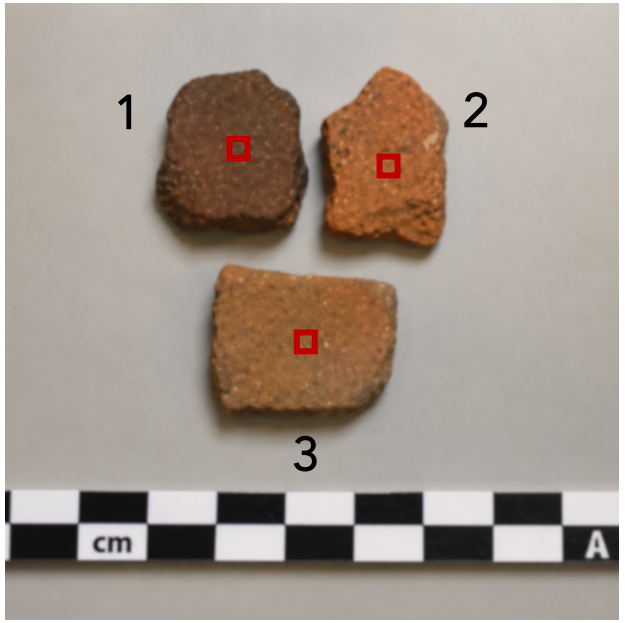


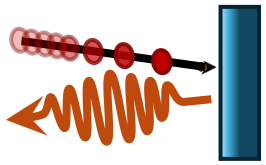
Protons
3 MeV

PIXE performed in vacuum
@ CNA Centro Nacional de Aceleradores

M.A. Respaldiza *et al.*, *Nucl. Instrum. Methods Phys. Res. B, 266:10* (2008)

Ceramic pot fragments – PIXE





Protons
3 MeV

PIXE performed in vacuum
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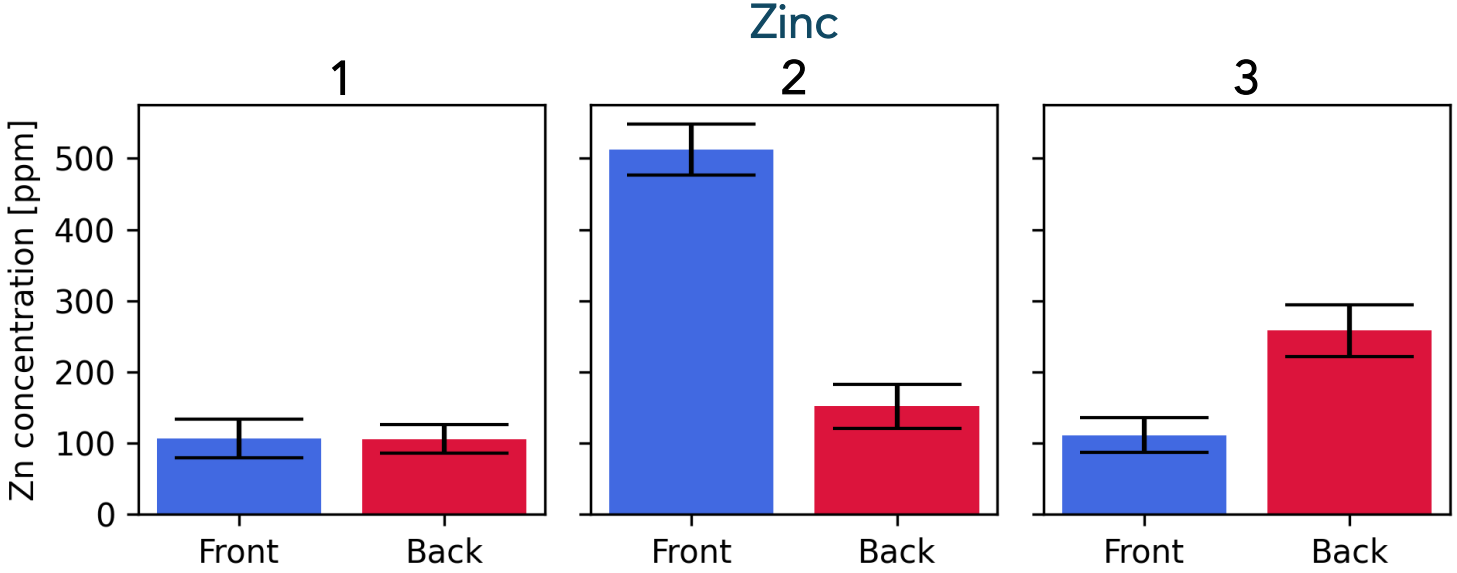
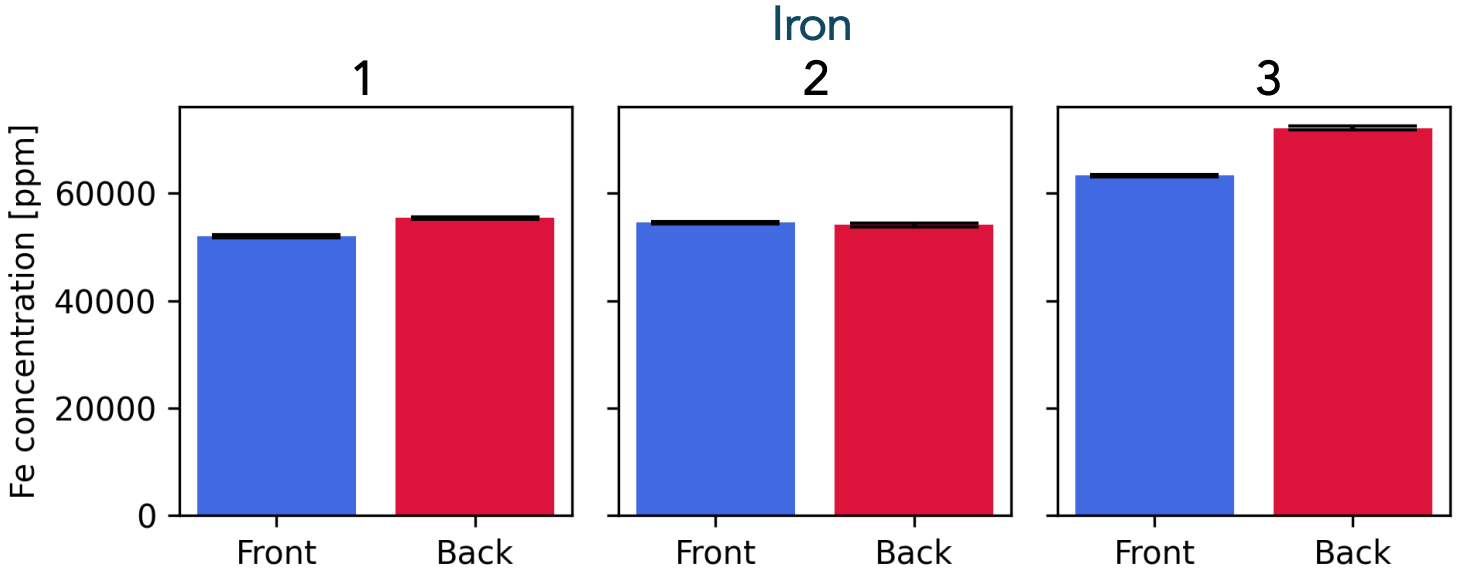
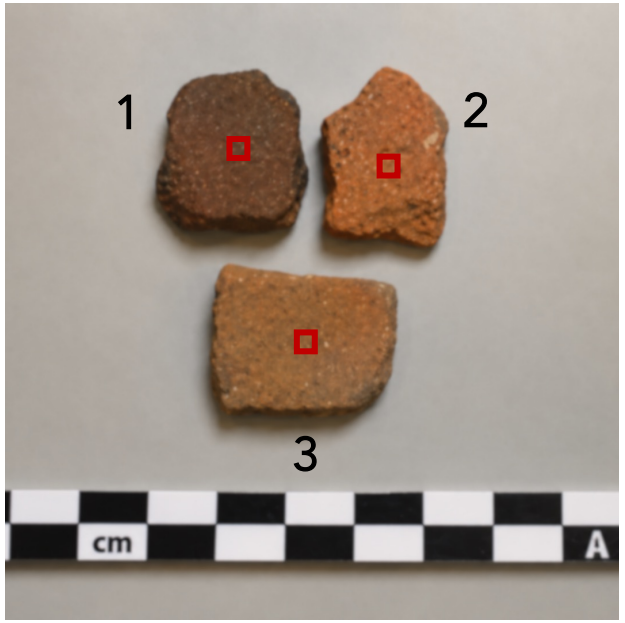


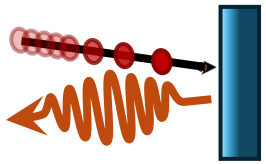


Low-concentration Zn (100 times less than Fe) linkable to brass production activities

M.A. Respaldiza *et al.*, *Nucl. Instrum. Methods Phys. Res. B, 266:10* (2008)

Ceramic pot fragments – PIXE





Protons
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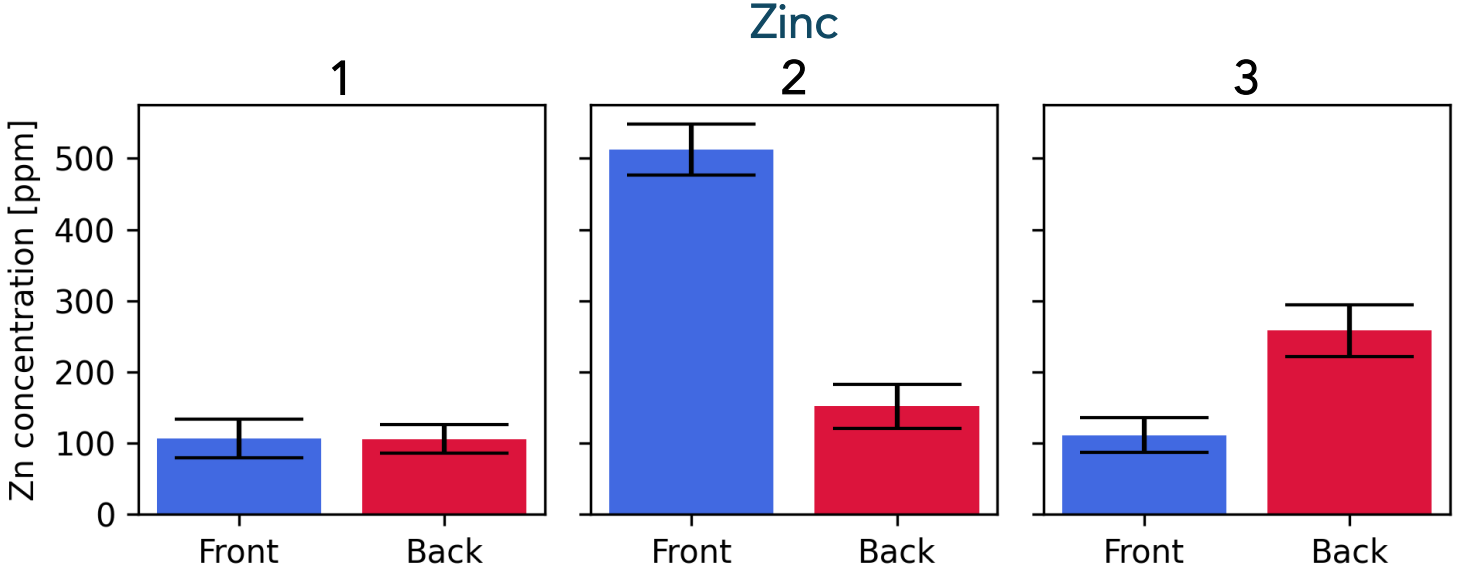
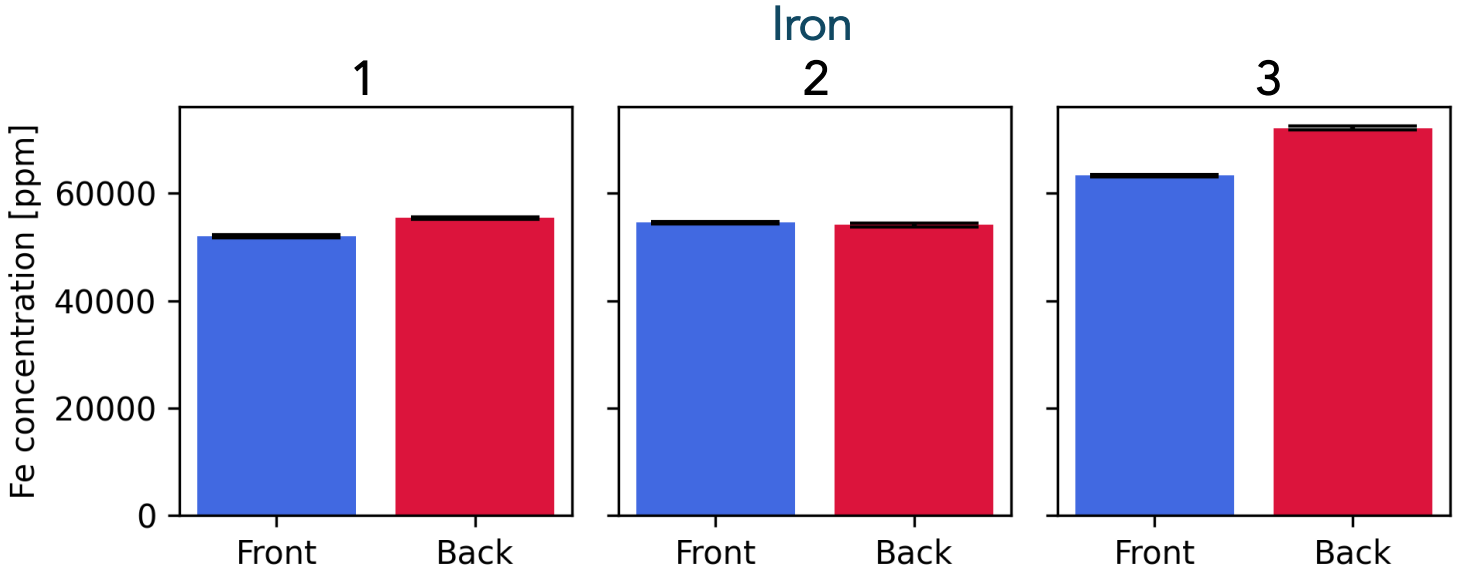
PIXE performed in vacuum
@ CNA Centro Nacional de Aceleradores



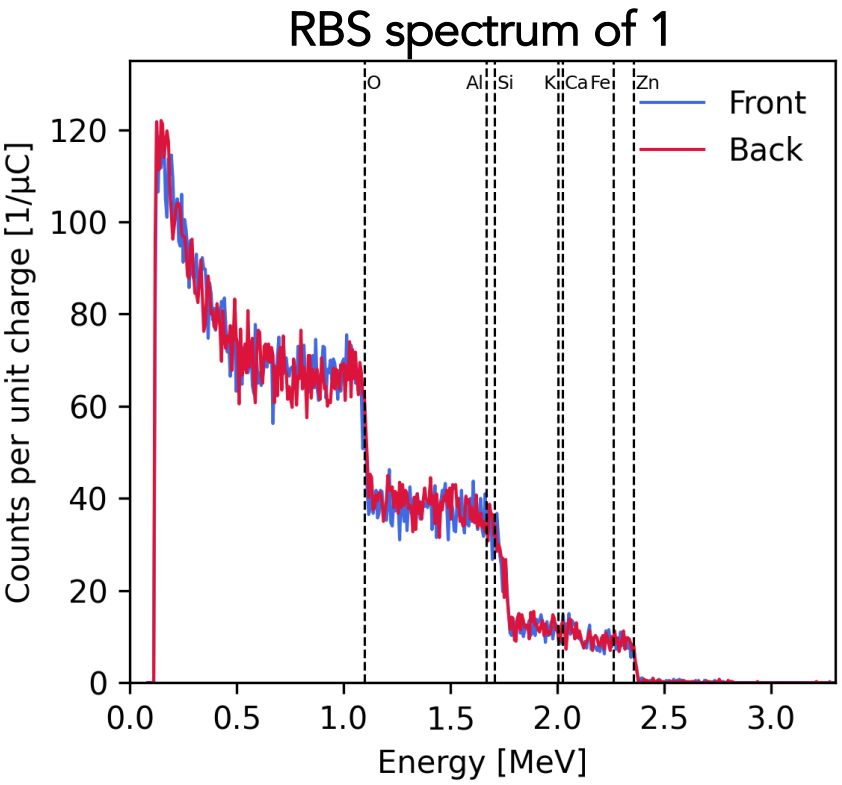


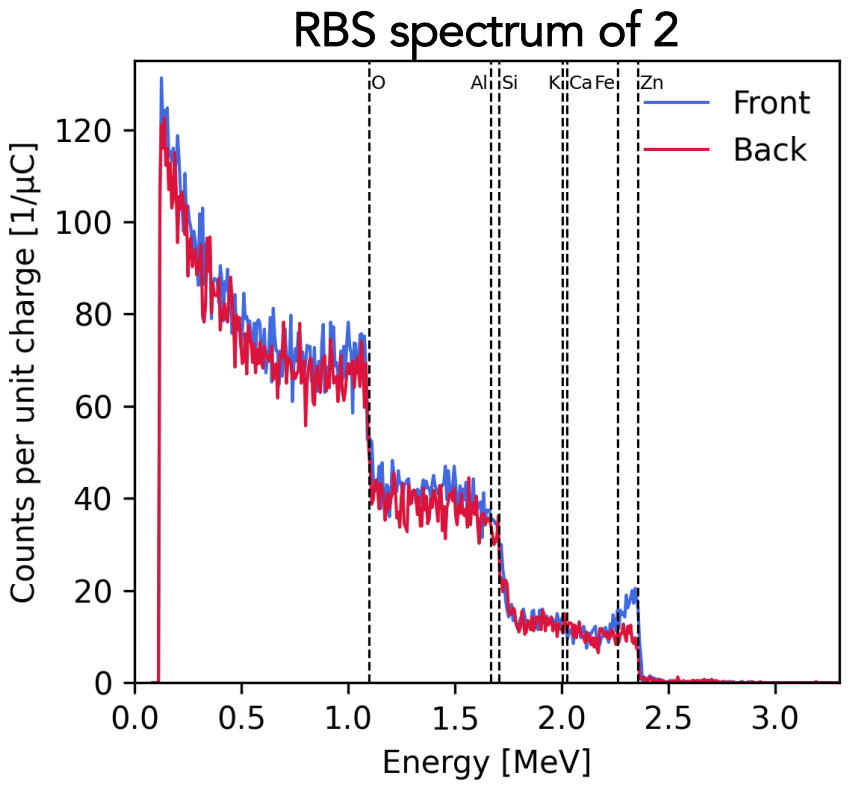
Low-concentration Zn (100 times less than Fe) linkable to brass production activities

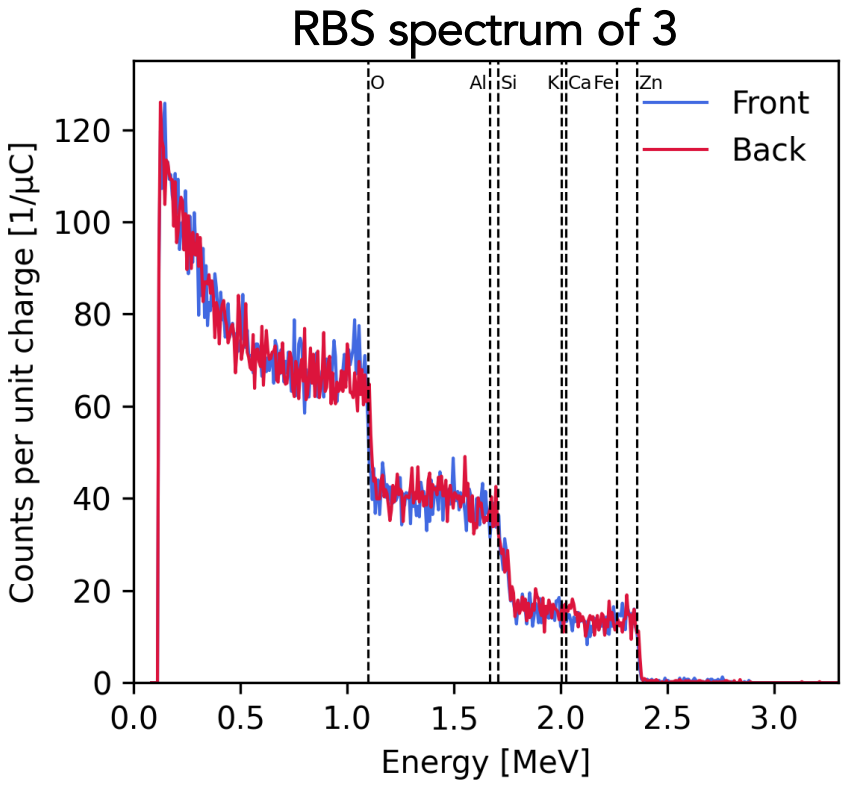
How can we be sure it is due to diffusion?

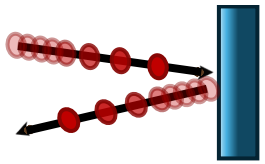
M.A. Respaldiza *et al.*, *Nucl. Instrum. Methods Phys. Res. B, 266:10* (2008)

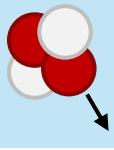
Ceramic pot fragments – RBS











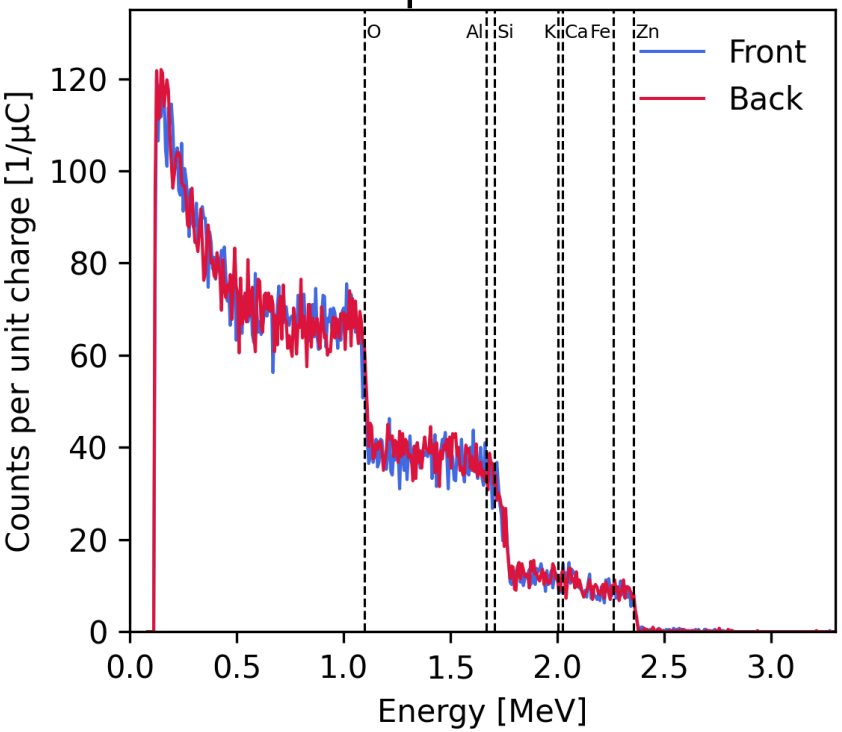
Alphas
3 MeV

RBS performed in vacuum
@ CNA Centro Nacional de Aceleradores

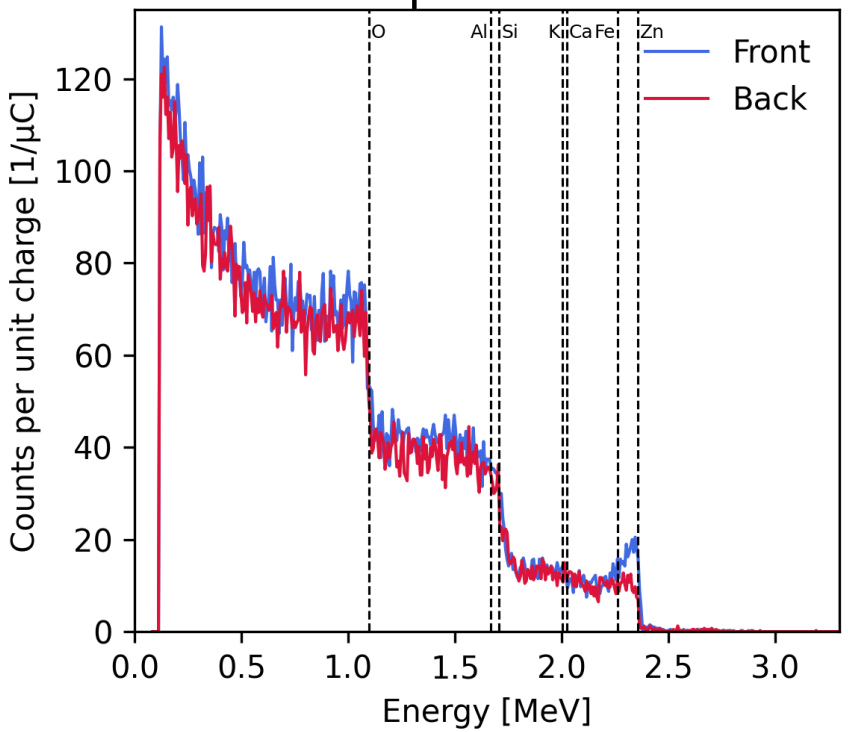
M.A. Respaldiza *et al.*, *Nucl. Instrum. Methods Phys. Res. B, 266:10* (2008)

Ceramic pot fragments – RBS

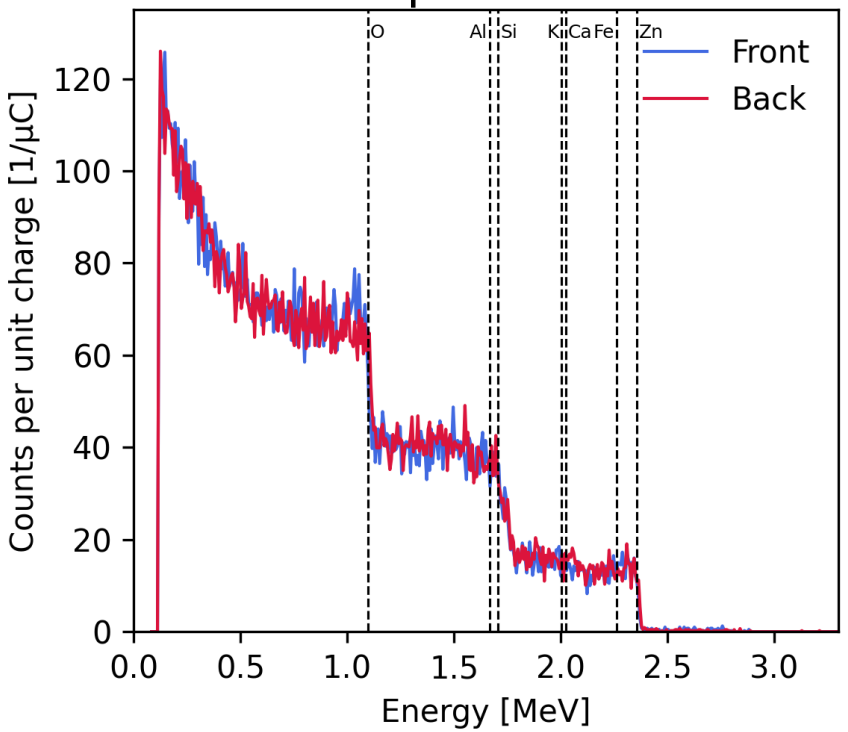
RBS spectrum of 1

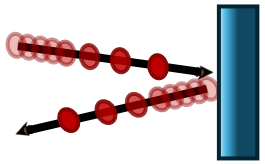


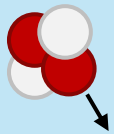
RBS spectrum of 2



RBS spectrum of 3







Alphas
3 MeV

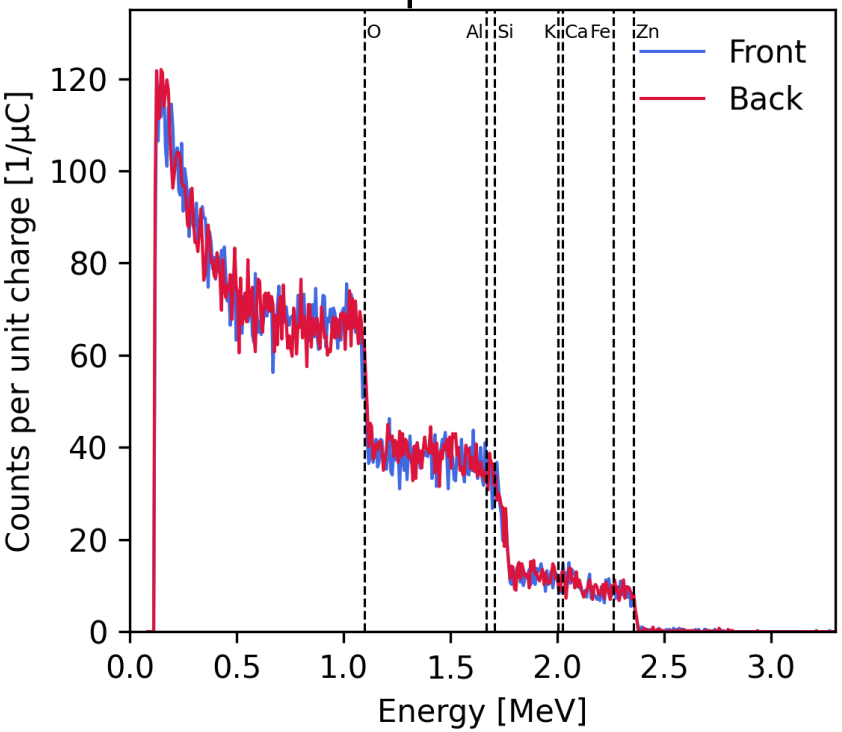
RBS performed in vacuum
@ CNA Centro Nacional de Aceleradores

Zn concentration **comparable** to **Fe** on surface

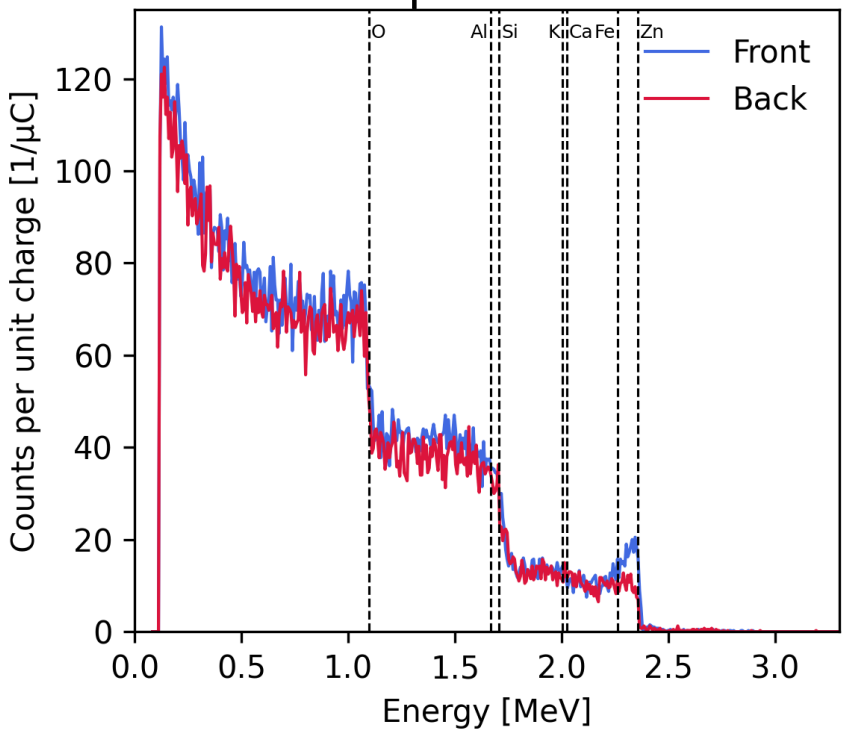
M.A. Respaldiza *et al., Nucl. Instrum. Methods Phys. Res. B, 266:10* (2008)

Ceramic pot fragments – RBS

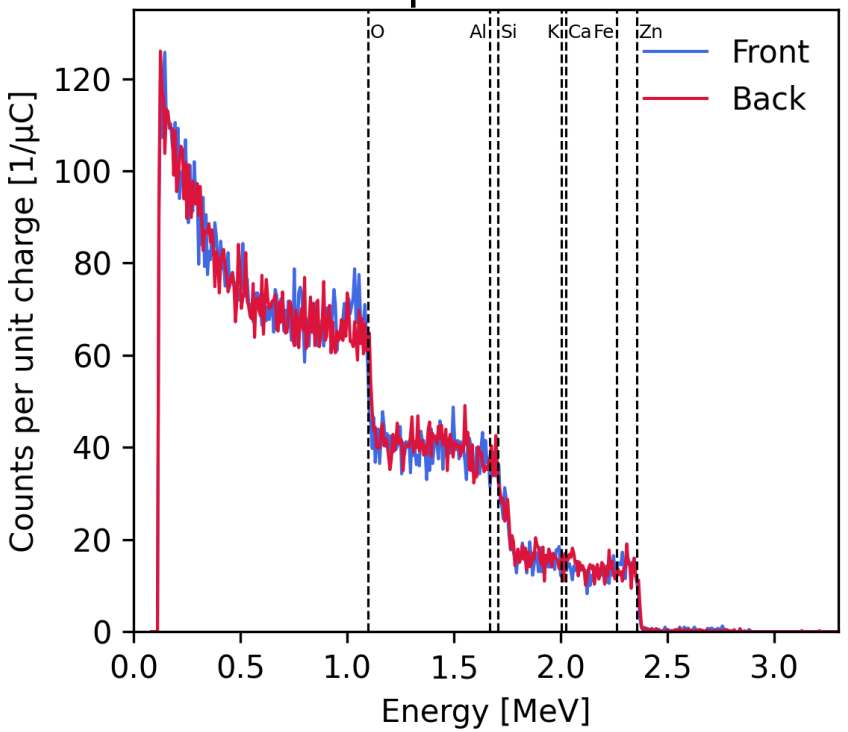
RBS spectrum of 1

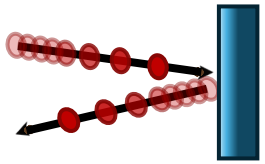


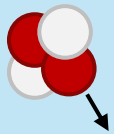
RBS spectrum of 2



RBS spectrum of 3







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RBS performed in vacuum
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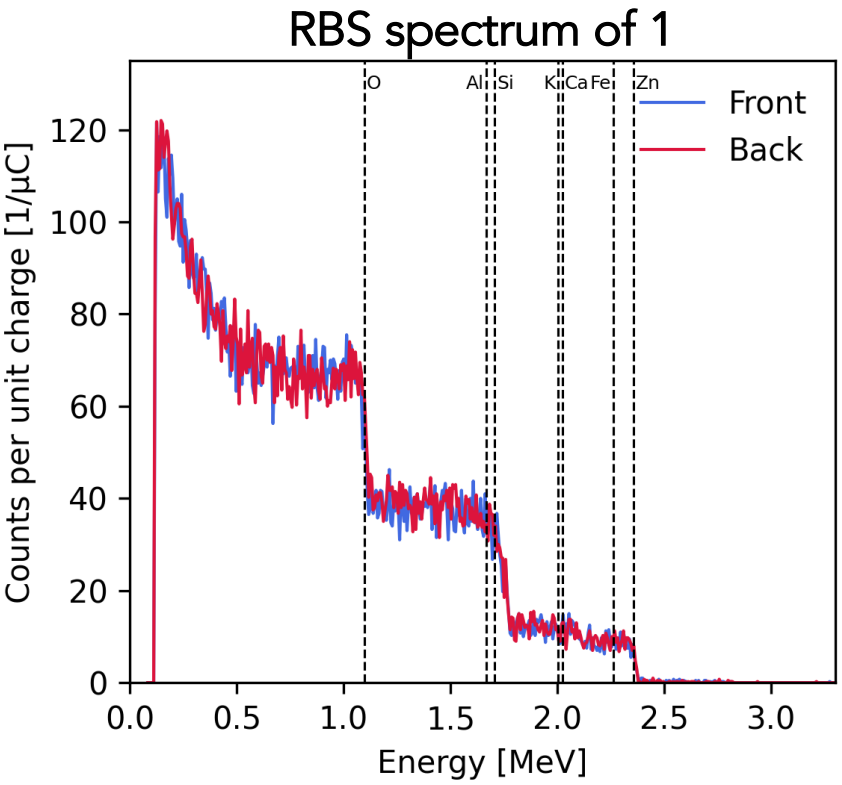
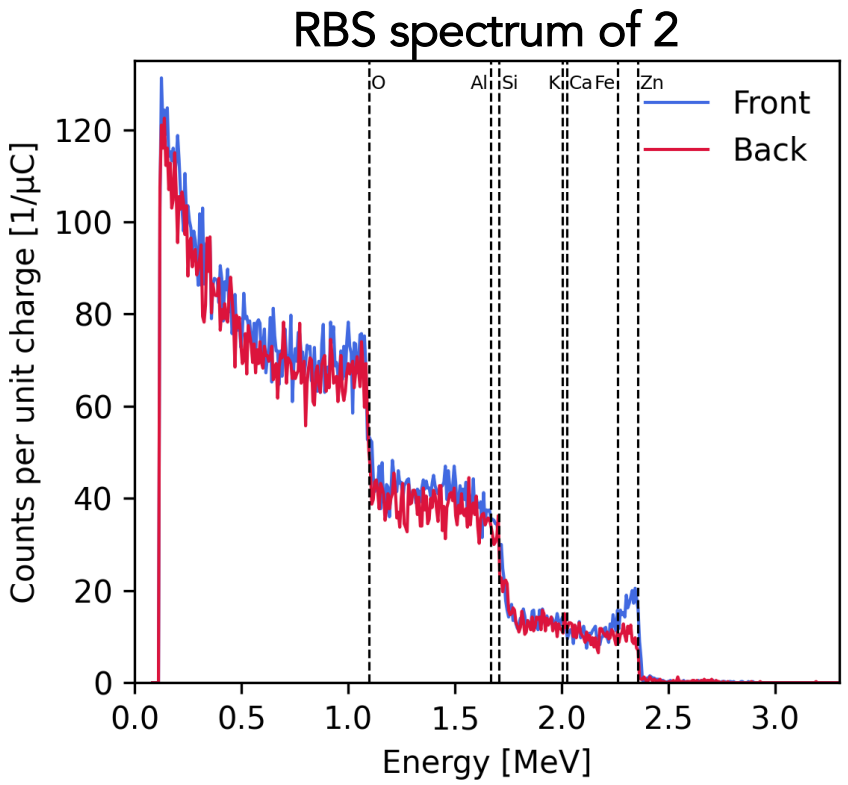
Zn concentration **comparable** to **Fe** on surface

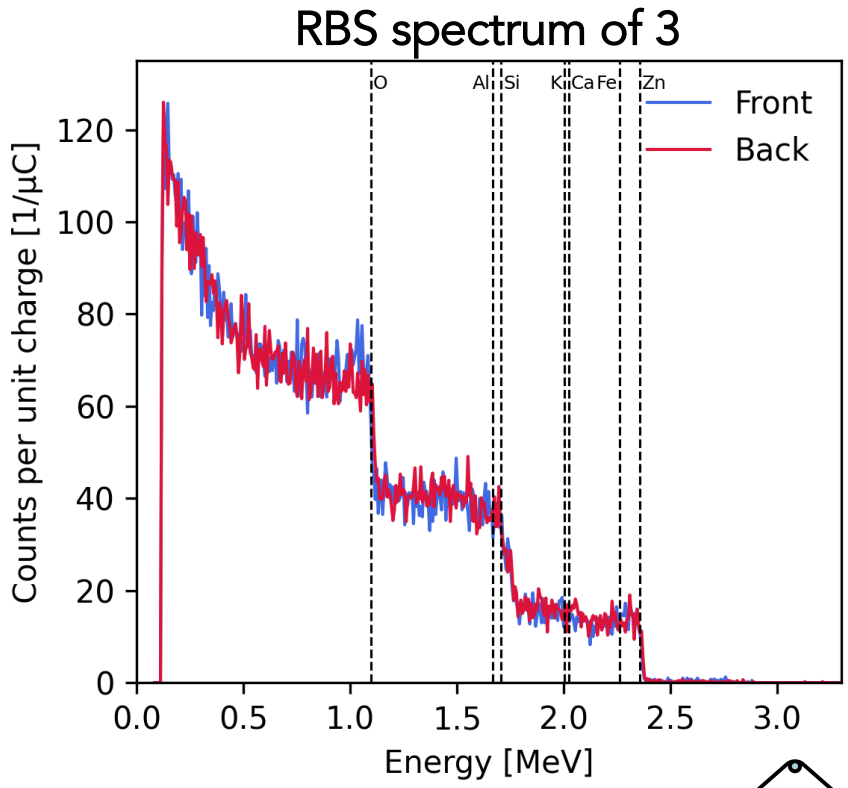
Zn RBS signal presents clear signs of diffusion in **2**

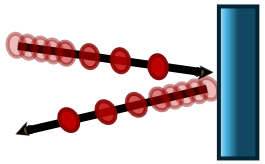
M.A. Respaldiza *et al., Nucl. Instrum. Methods Phys. Res. B, 266:10* (2008)

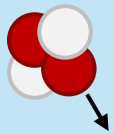
Ceramic pot fragments – RBS











Alphas
3 MeV

RBS performed in vacuum
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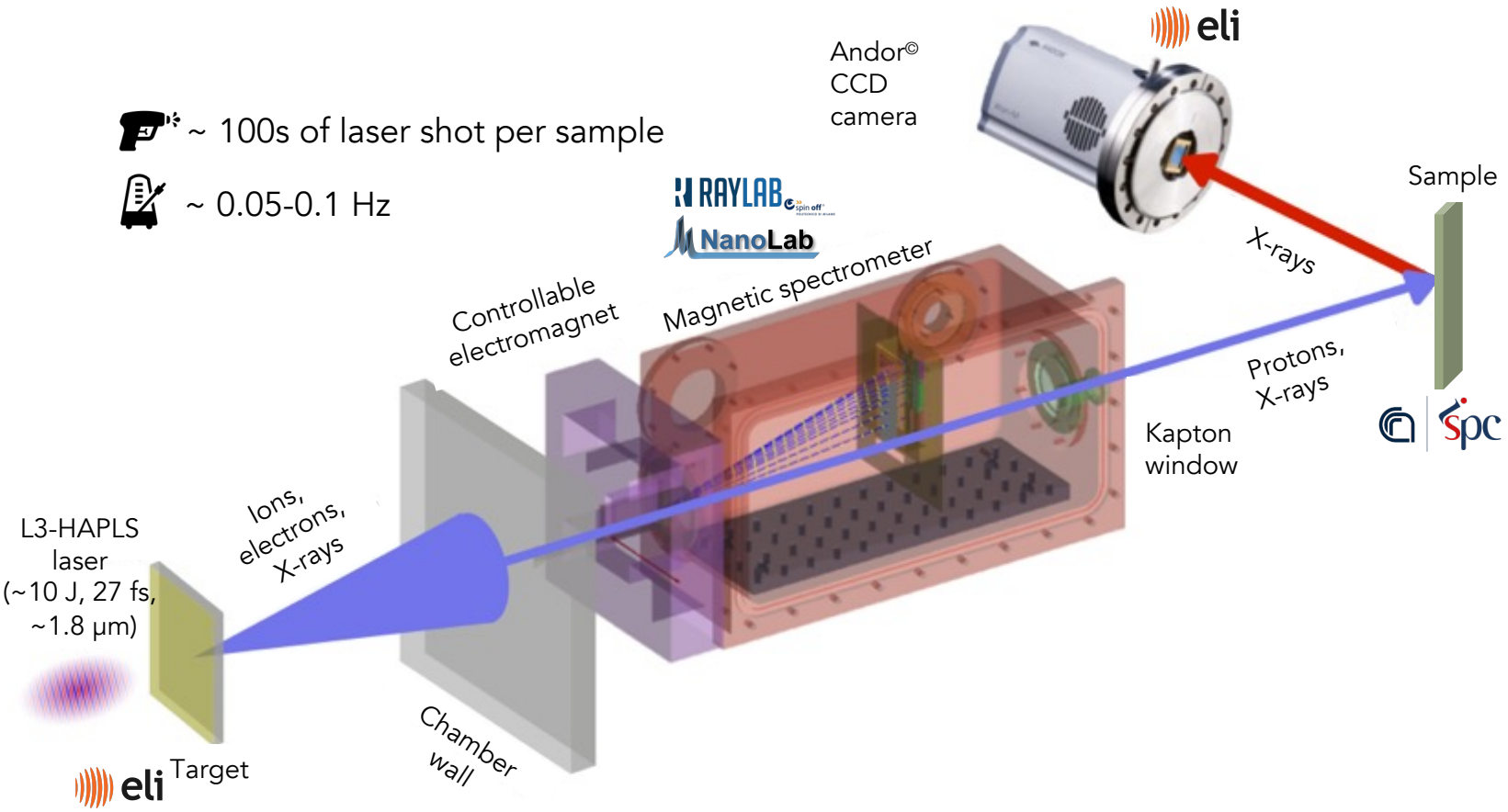
Zn concentration **comparable** to **Fe** on surface

Zn RBS signal presents clear signs of diffusion in **2**

Assess the **Zn penetration** to confirm the diffusion hypothesis through SIMNRA simulations

M.A. Respaldiza *et al., Nucl. Instrum. Methods Phys. Res. B, 266:10* (2008)

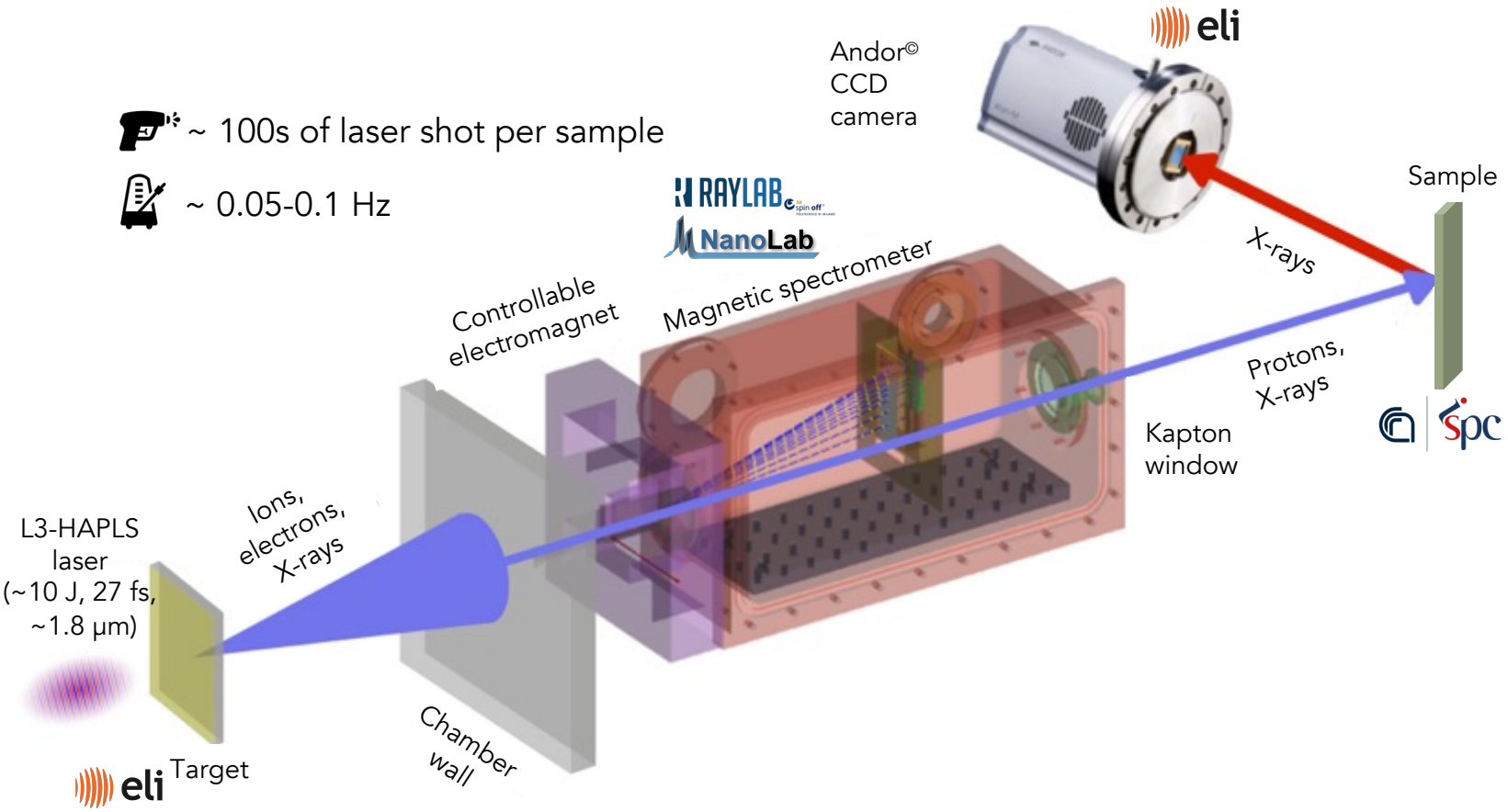
Ceramic pot fragments – laser-based PIXE



Test of **laser-driven ion sources** for **non-invasive material analysis** in cultural heritage.

M. Passoni *et al.*, *P.R.L.*, *101:115001* (2008)
F. Mirani *et al.*, *Sci. Adv.*, *7:eabc8660* (2021)
K. Ambrogioni *et al.*, *under review at Sci. Adv.* (2026)

Ceramic pot fragments – laser-based PIXE



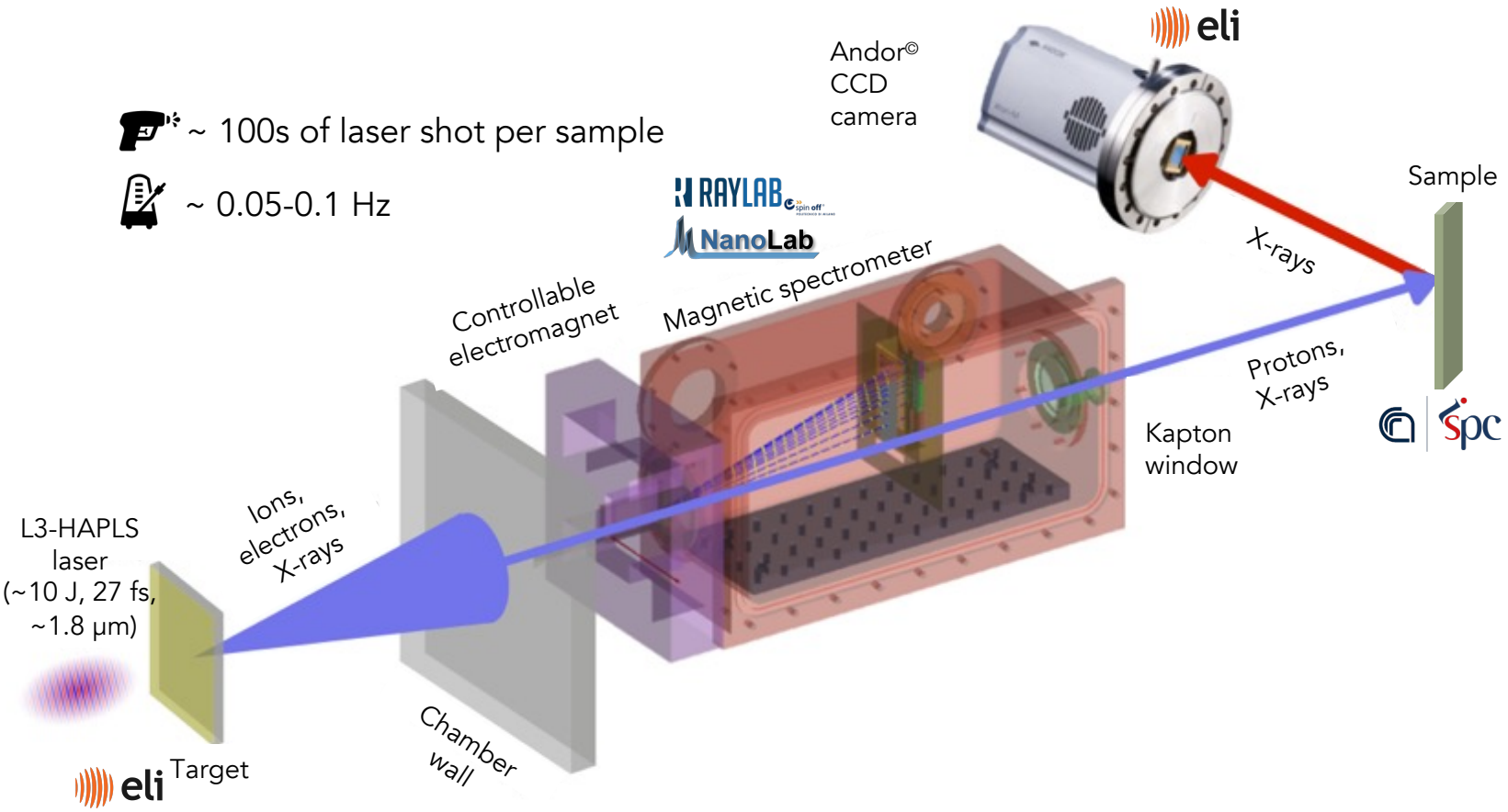
Test of **laser-driven ion sources** for **non-invasive material analysis** in cultural heritage.

Compact and possibly **transportable** acceleration scheme

Cost effectiveness for laboratory scale ion sources

M. Passoni *et al., P.R.L., 101:115001 (2008)*
F. Mirani *et al., Sci. Adv., 7:eabc8660 (2021)*
K. Ambrogioni *et al., under review at Sci. Adv. (2026)*

Ceramic pot fragments – laser-based PIXE



Test of **laser-driven ion sources** for **non-invasive material analysis** in cultural heritage.

Compact and possibly **transportable** acceleration scheme

Cost effectiveness for laboratory scale ion sources

Non-monoenergetic energy spectrum for ions

M. Passoni *et al., P.R.L., 101:115001 (2008)*
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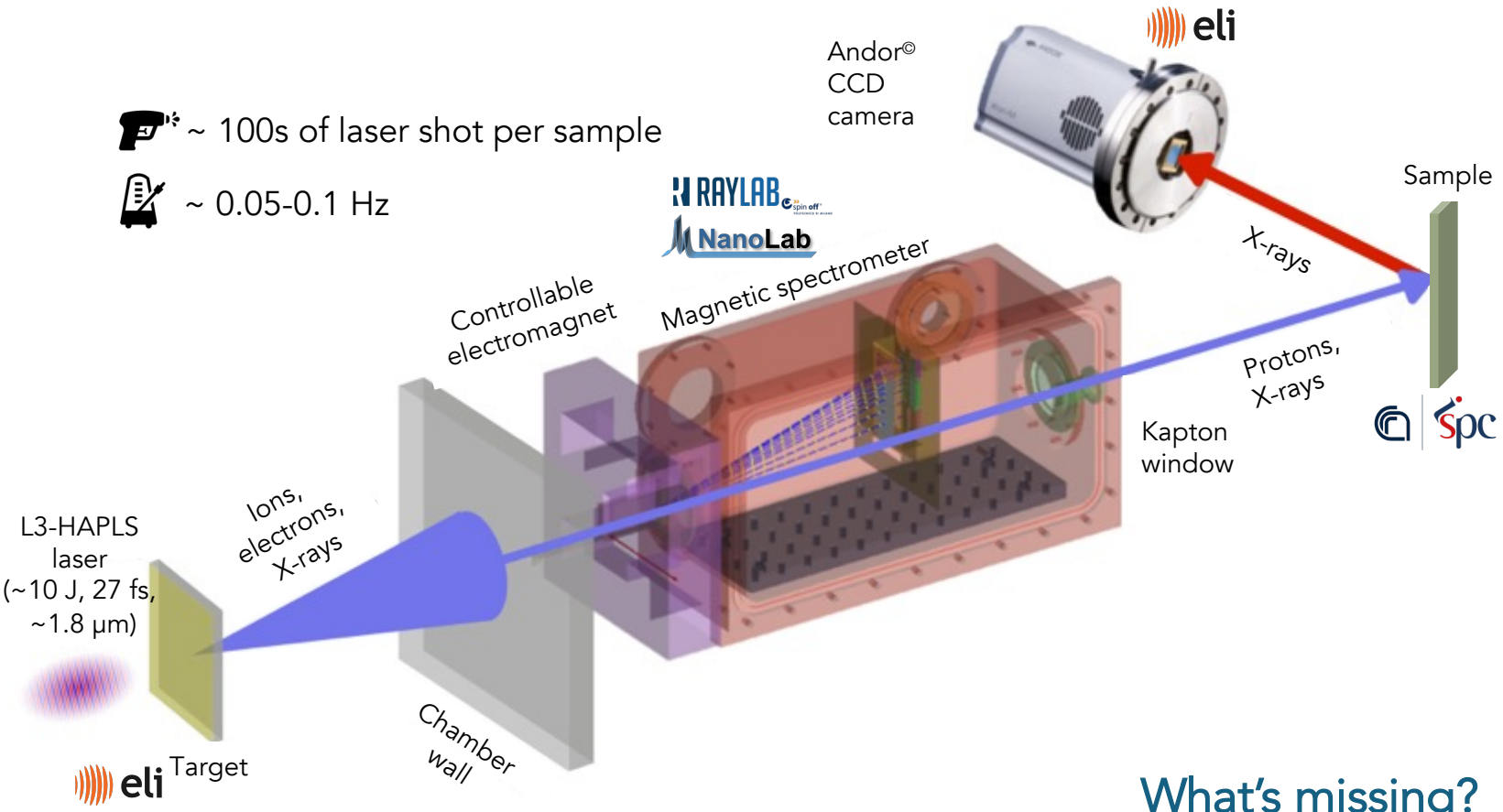

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Compact and possibly **transportable** acceleration scheme

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What's missing?

Tools for quantitative analysis of laser-based PIXE spectra

Compact and **characterised** setup for **in-air** irradiation

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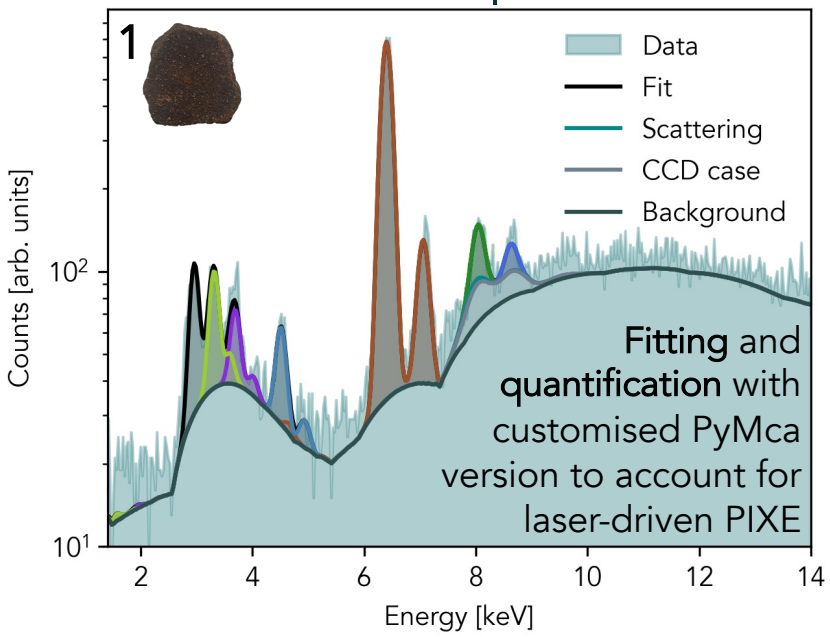
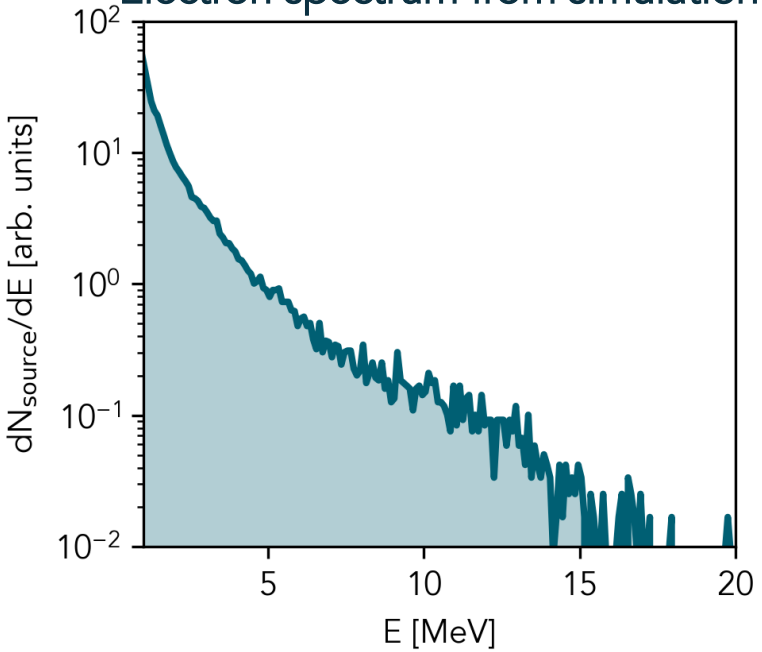
Ceramic pot fragments – laser-based PIXE

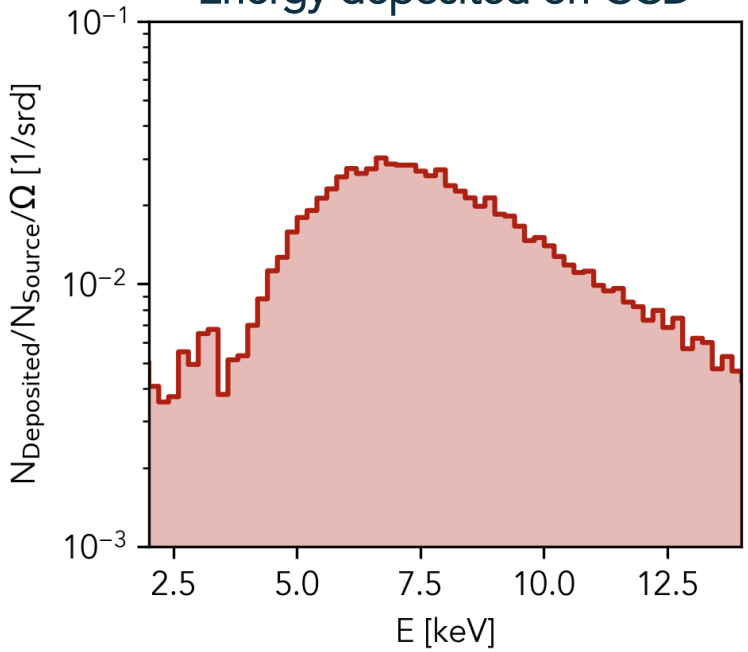
PIXE+XRF spectrum



Electron spectrum from simulation



Energy deposited on CCD



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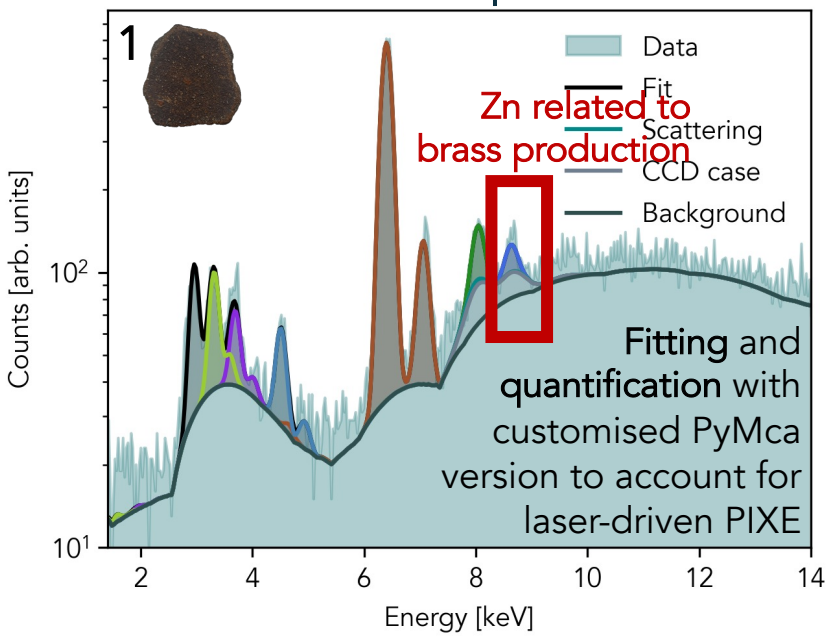

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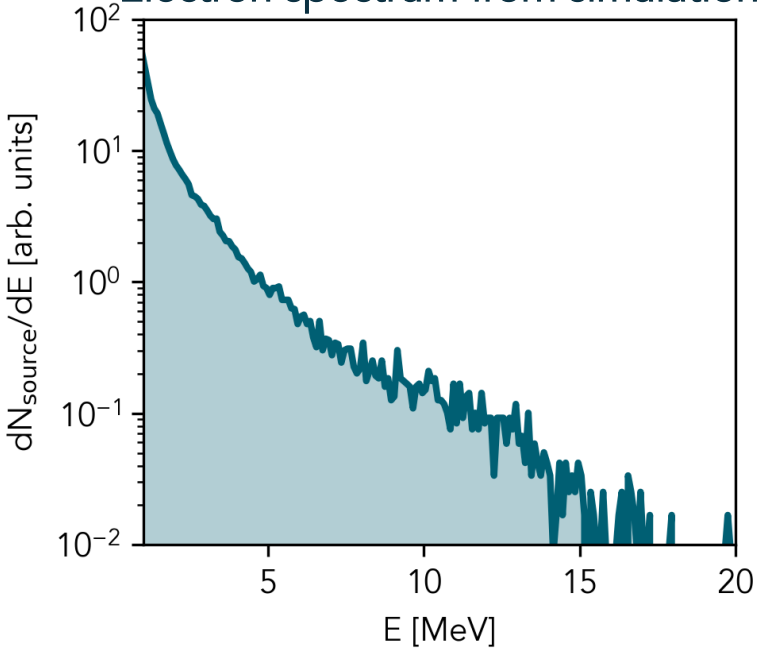

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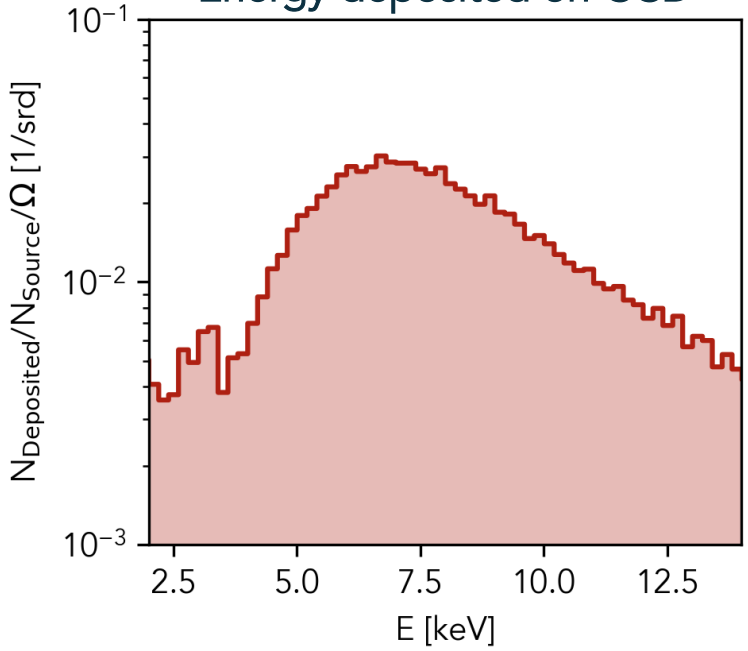

GEANT4 and Smilei simulations to find **cause of background**

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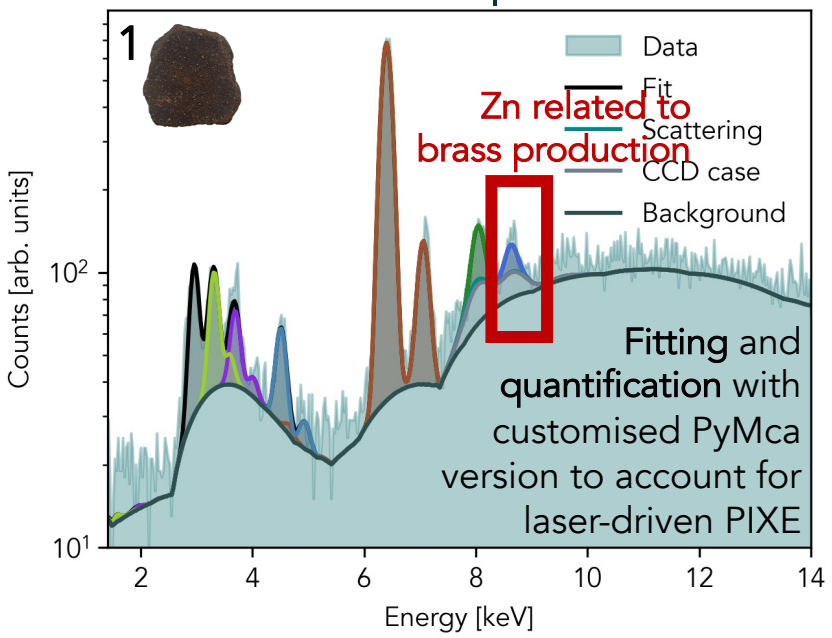

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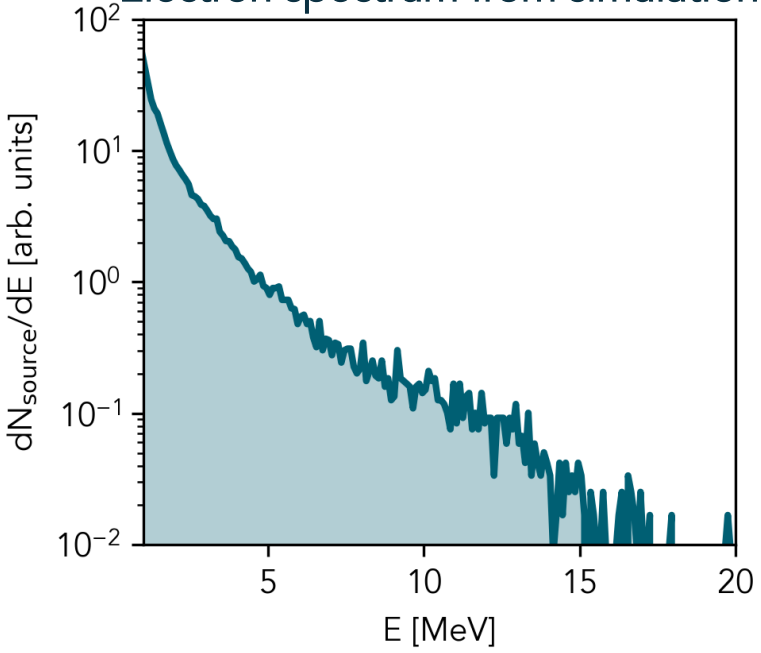

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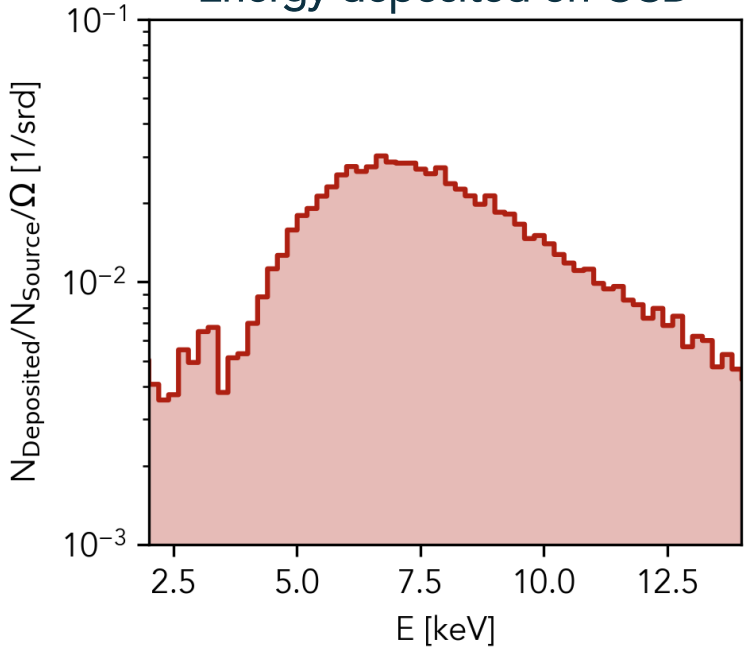

GEANT4 and Smilei simulations to find **cause of background**

Electrons impinging on CCD screen

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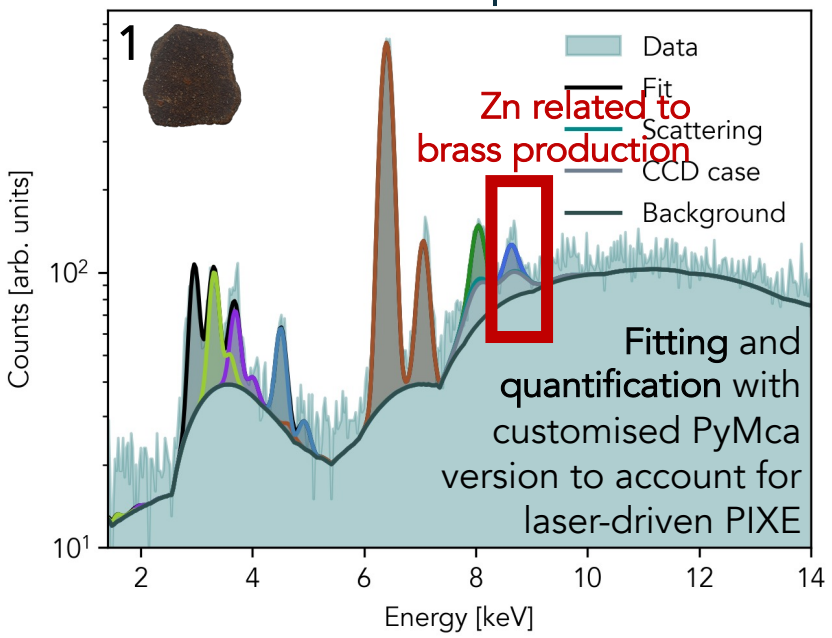

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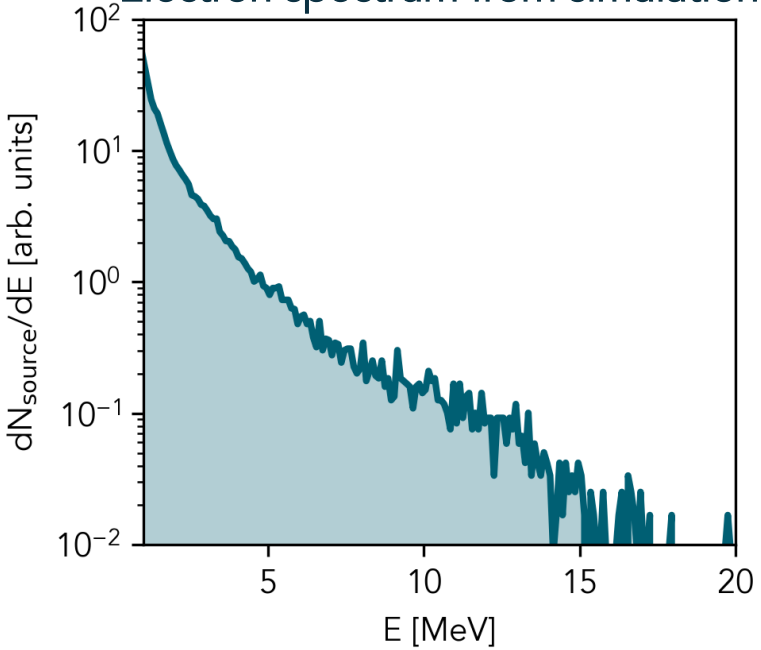

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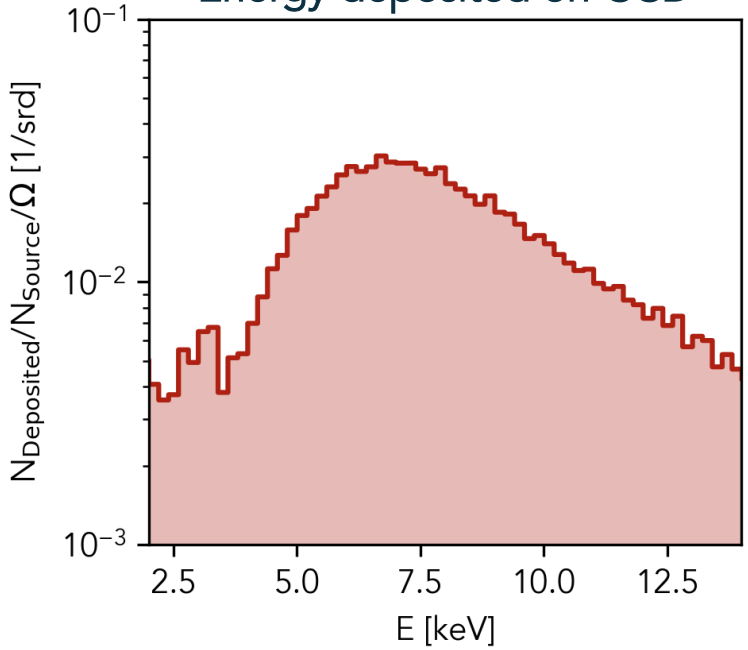

GEANT4 and Smilei simulations to find **cause of background**

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WORK IN PROGRESS

- **Mitigation** of background source
- Use of **He flux** to reduce in-air attenuation below 3 keV
- Use of alternative **CCDs** with higher efficiency above 10 keV

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Ceramic pot fragments – Summary of the results

Observed presence of elements in the ceramic related to **brass production** (Zn)

Non-invasively observed Zn diffusion in ceramic bulk demonstrating the presence of **brass production** in iron-age Mediolanum

Tested **non-conventional ion sources** for non-invasive material analysis applications and addressed **improvement strategies**

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Connected to ceramic technological use

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Tested **non-conventional ion sources** for non-invasive material analysis applications and addressed **improvement strategies**

Assess Zn diffusion in all fragments through **simulations**

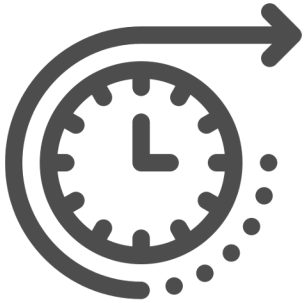
Development of an improved setup for **laser-based PIXE**

Conclusions and future perspectives

Assessed **non-invasive advanced** multi-technique protocol for studying **archaeological ceramic artifacts**

Non-invasively determined features of the glazing production in late Roman Mediolanum

Non-invasively determined proofs of the brass production in iron-age Mediolanum



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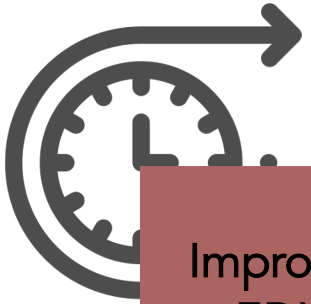

Improvement of the SEM-EDX measures for Cu function determination

Further analysis of RBS spectra to confirm Zn diffusion in the ceramic bulk

Improvement of the setup for improved reliability of results from **non-conventional ion sources**

Acknowledgments

- Our research line group @ NanoLab


M. Passoni


V. Russo


D. Dellasega


A. Maffini


F. Mirani


D. Orecchia


K. Ambrogioni


M. S. Galli De Magistris


M. Iaccarino


D. Vavassori

- The collaboration with nuclear instrumentation and measurements group @ POLITECNICO MILANO 1863 :
  - *Andrea Pola* (team leader), *Davide Mazzucconi*, *Francesco Casamichiela*, *Aixeen Fontanilla*
- The collaboration with RAYLAB spin off company
  - *Dario Rastelli*
- The eli Beamlines facility
  - Access to **ELIMAIA beamline** through 5th User call
  - The **ELIMAIA internal team**: *Vasiliki Kantarelou*, *Francesco Schillaci*, *Lorenzo Giuffrida* and *Daniele Margarone*
- The **institute of heritage science** teams from:
  - Milan: *Claudia Conti* (Raman Lab team leader), *Elisa Maria Grassi* (Archaeologist)
  - Catania: *Francesco Paolo Romano* (X-Ray Lab team leader), *Claudia Caliri*, *Eva Luna Ravan*
- The CNA Centro Nacional de Aceleradores facility (*Miguel Ángel Respaldiza*, *Inés Ortega Feliu*, *Blanca Gómez-Tubio*)

Thank you for your attention!

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PyMca modified workflow for PIXE