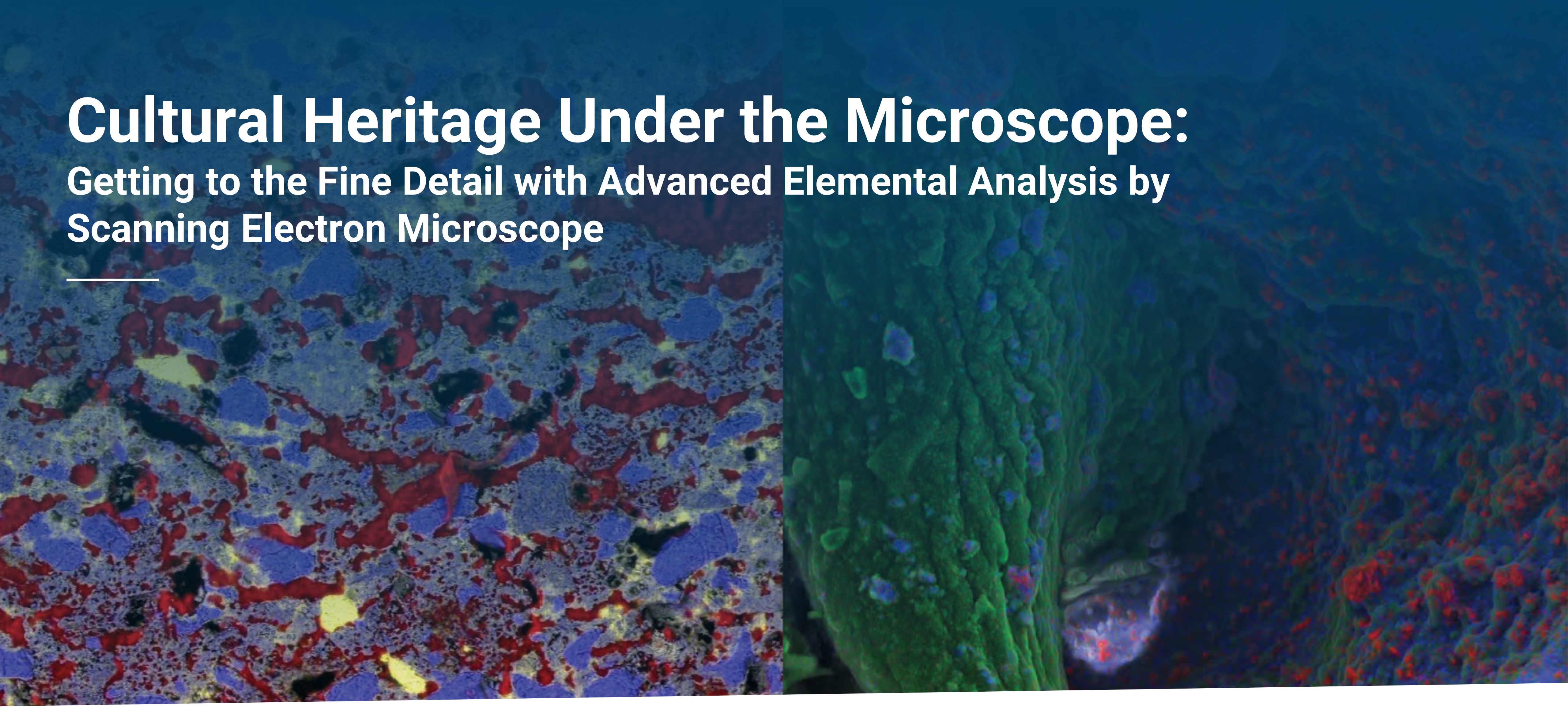
Cultural Heritage Under the Microscope:

Getting to the Fine Detail with Advanced Elemental Analysis by Scanning Electron Microscope

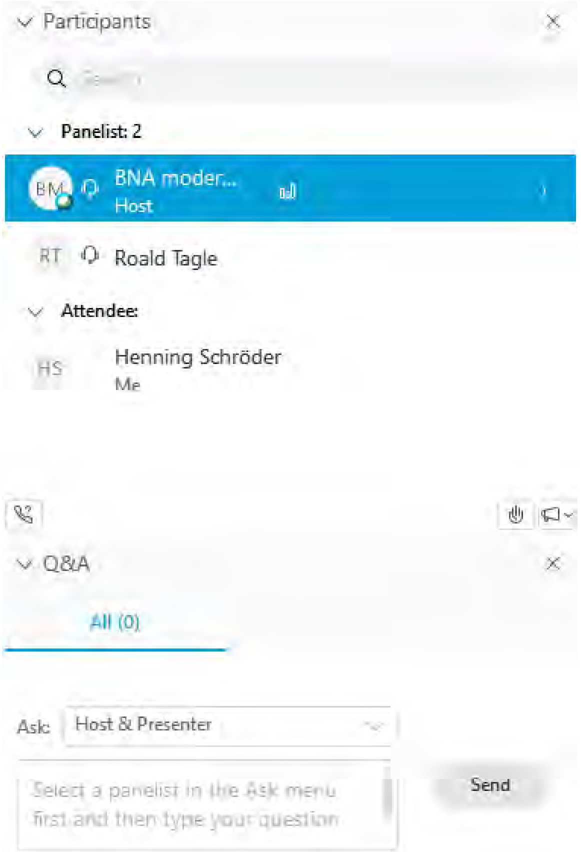


Art & Conservation Webinar Series
Cultural Heritage Under the Microscope

If you have questions during this webinar, please **type your questions**, thoughts, or comments in the **Q&A box** and **press Send**.

We ask for your understanding if we do not have time to discuss all comments and questions within the session.

Any unanswered questions or comments will be answered and discussed by e-mail or in another WebEx session.



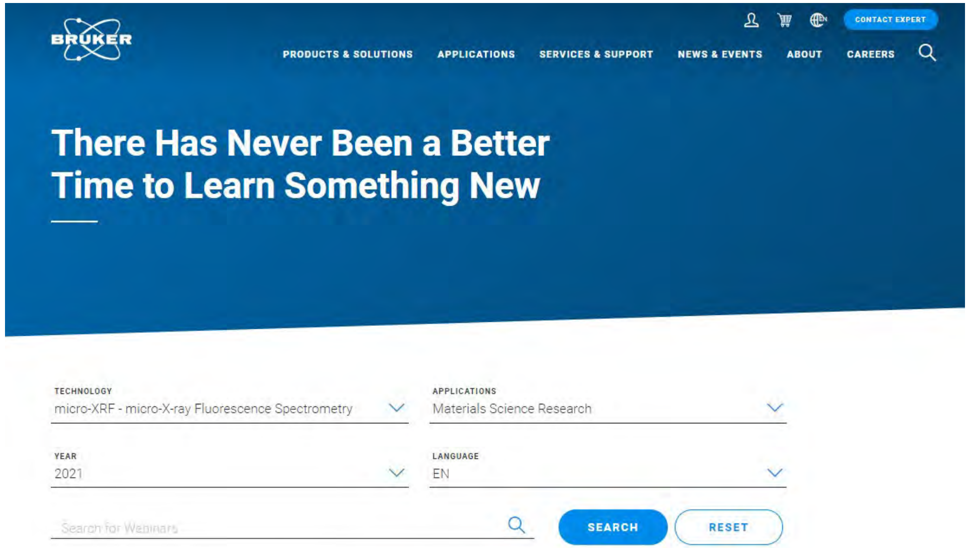
Art & Conservation Webinar Series
On-demand and upcoming

Currently available on-demand at www.bruker.com

- ELIO, Portability and Flexibility in Art Studies – Hear our Experts' Voice
- XRF Data Processing in Art and Conservation with ESPRIT Reveal
- TRACER: The Benchmark in Handheld-XRF for Cultural Heritage
- New Horizons of micro-XRF in Art and Conservation
- Flexible and portable XRF mapping solutions for Art and Conservation: Bruker’s ELIO and CRONO spectrometers

Coming soon

- The M6 JETSTREAM in Art & Conservation – a view from the field
- Approaching analysis by Handheld-XRF in cultural heritage studies (3 events)



SEM-EDS analysis in Cultural Heritage studies

Max Patzschke
Application Scientist EDS

Bruker Nano Analytics
Berlin, Germany

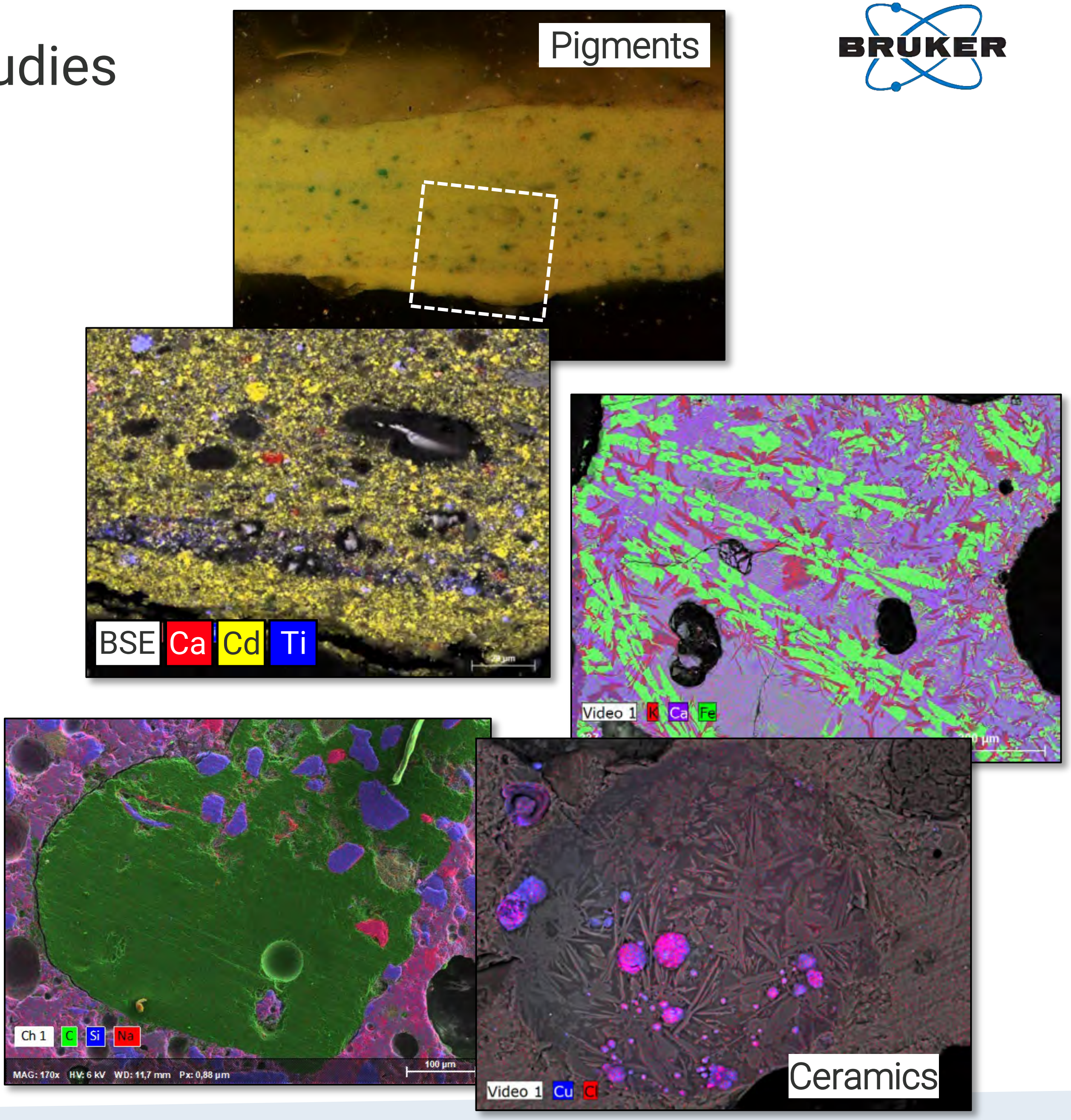
Dr. Nigel Kelly
Senior Market Applications Scientist

Bruker Nano Analytics
Denver, CO, USA

SEM-EDS analysis in Cultural Heritage studies
Why Scanning Electron Microscopy?

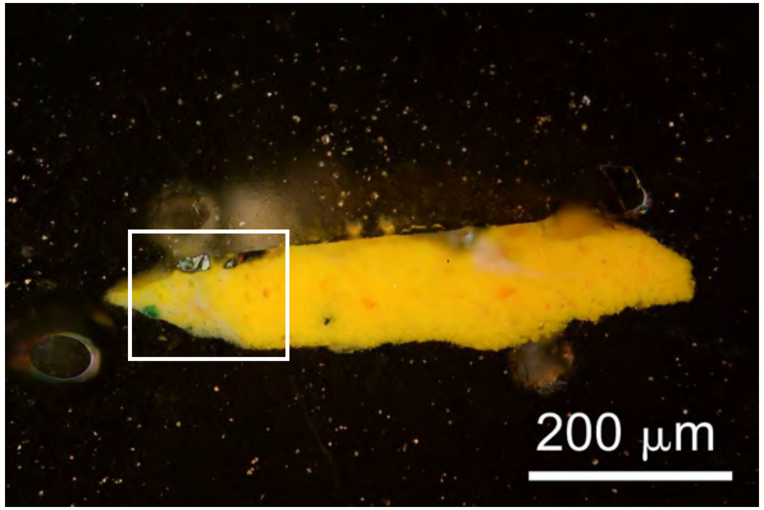
- The high spatial resolution afforded by SEM analysis makes this technique the standard for many areas of characterization and research in cultural heritage
  - Imaging (e.g., SE, BSE)
  - 1-D and 2-D elemental analysis (e.g., EDS, WDS)
  - Structural analysis of natural and synthetic materials (e.g., EBSD)

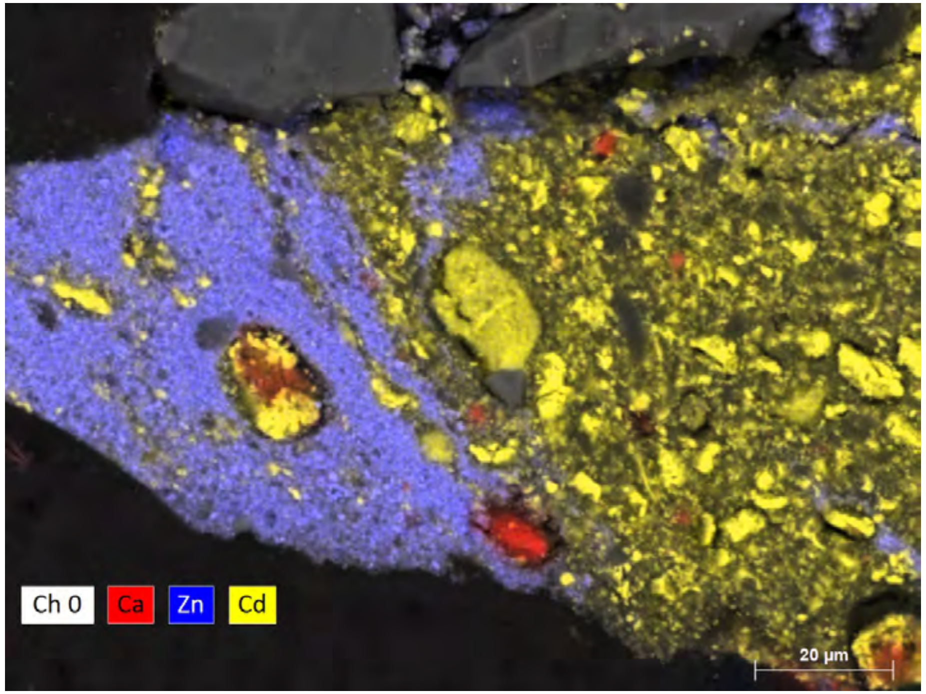
- Application areas
  - Ceramics
  - Archaeometallurgy
  - Stone tools and obsidian sourcing
  - Pigment and paint analysis

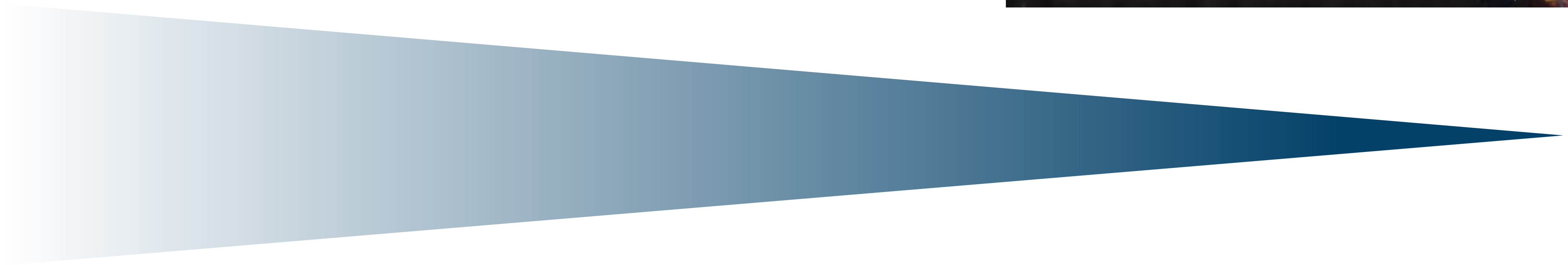


Focusing the analytical workflow

Giovanni Maimeri, *Trigliee acciughe*

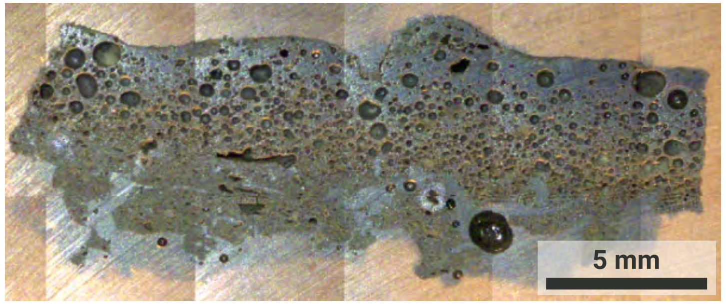


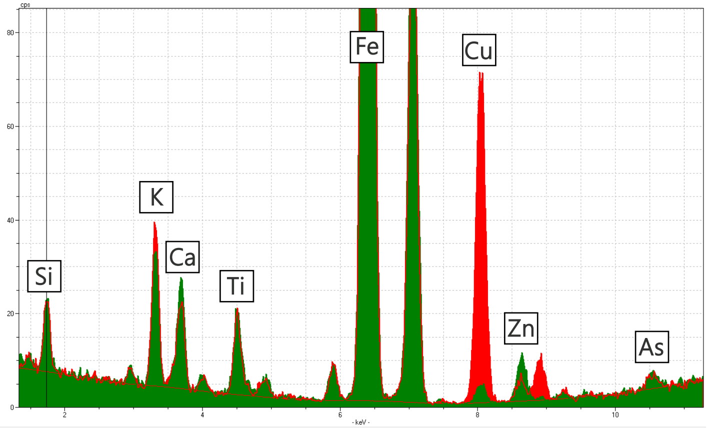




Focusing the analytical workflow

HH-XRF

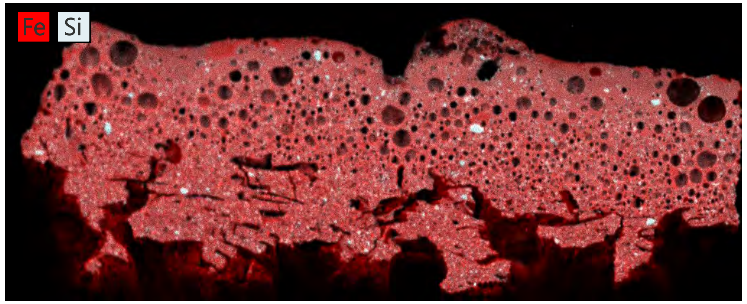


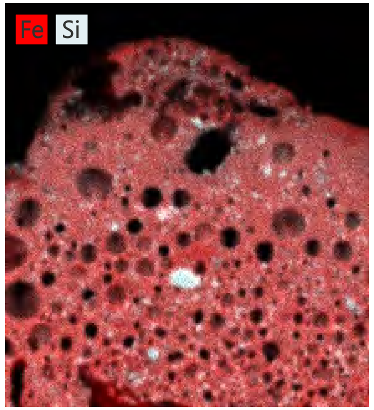


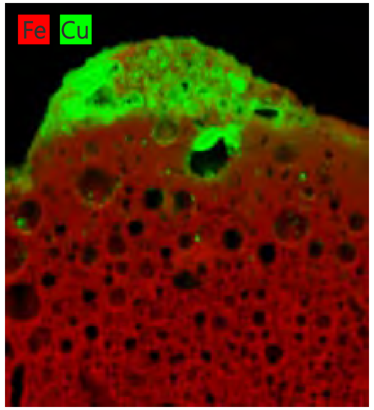
Compositional average of 3-8 mm spot area

Bulk analysis / Surface coatings / Mixtures

µXRF / MA-XRF



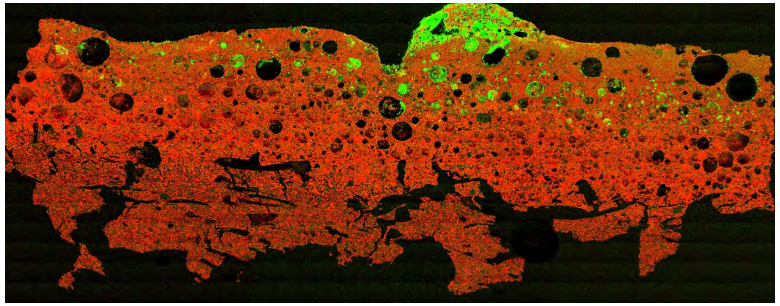


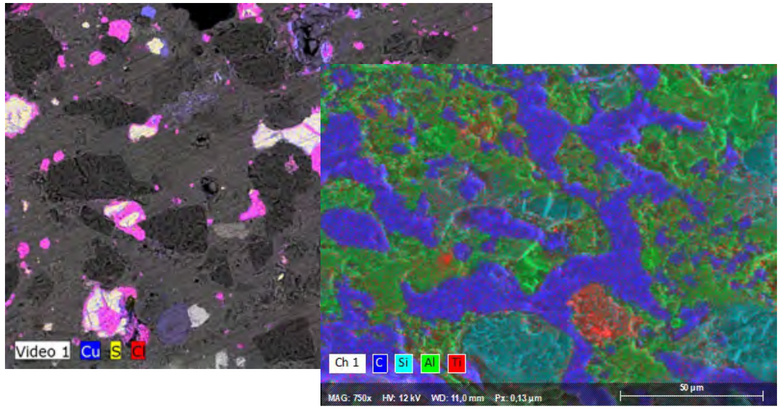


High-resolution at single spot (2mm – <20 µm), 2-D mapping

Fine features / Spatial variations / Mixture due to information depth

SEM-EDS





Highest resolution at the scale of ~µm – nm spot

Extraction detail of finest features / Spatial compositions

SEM-EDS analysis in Cultural Heritage studies
Webinar Outline

- Brief introduction to Energy Dispersive Spectroscopy using the Scanning Electron Microscope

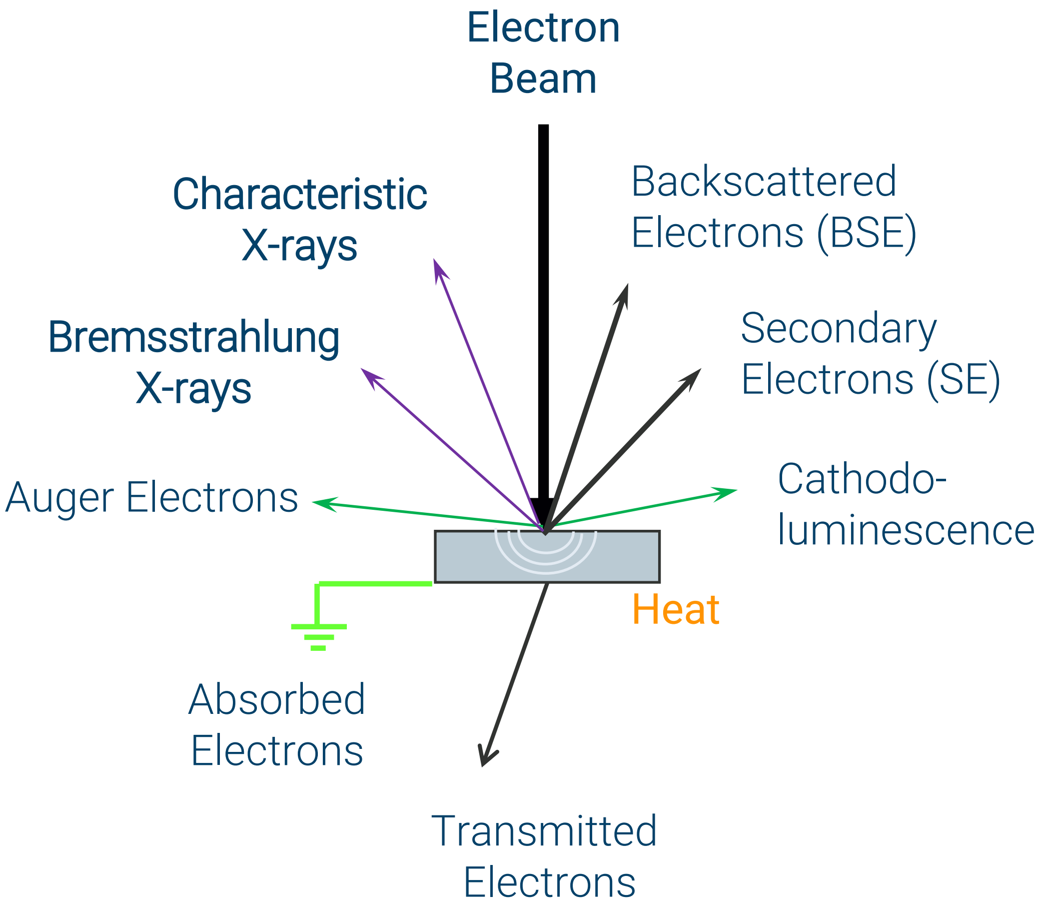
- Three examples of use in cultural heritage studies
  - Archaeological ceramics (furnace crucibles)
  - Paint cross-sections
  - Obsidian artefact analysis by SEM-based micro-XRF

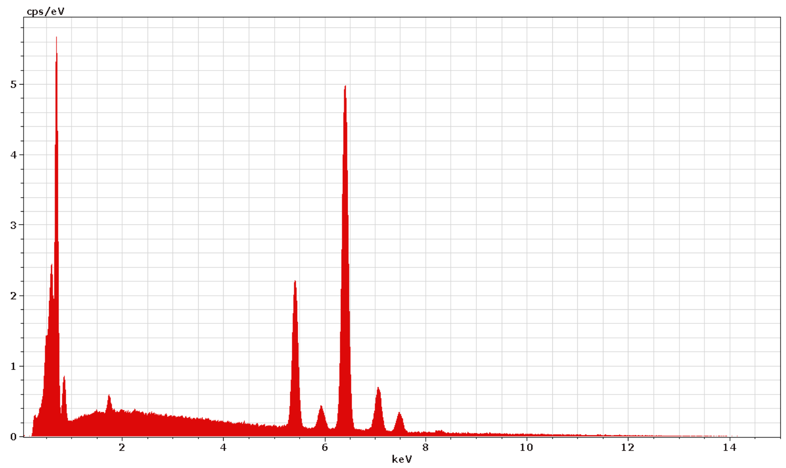
    (based on work of Meredith Sharp & others at the Smithsonian Institution)

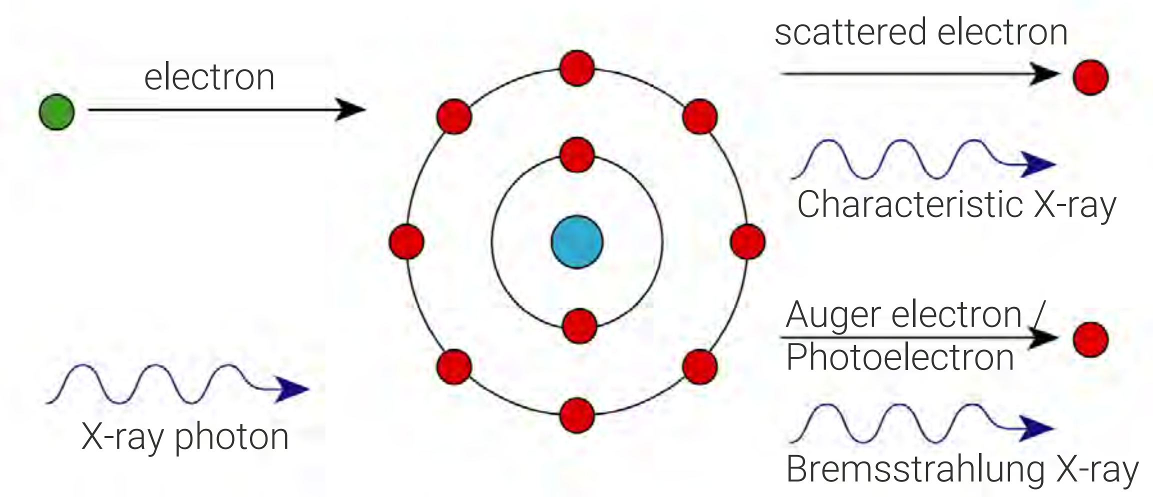
Bruker Scanning Electron Microscope Analyzers
Our “evolving eyes”

- **µXRF**: Micro X-ray Fluorescence
- **WDS**: Wavelength Dispersive Spectroscopy
- **EBSD**: Electron Backscatter Diffraction
- **EDS / EDX**: Energy Dispersive Spectroscopy

Beam – specimen interaction

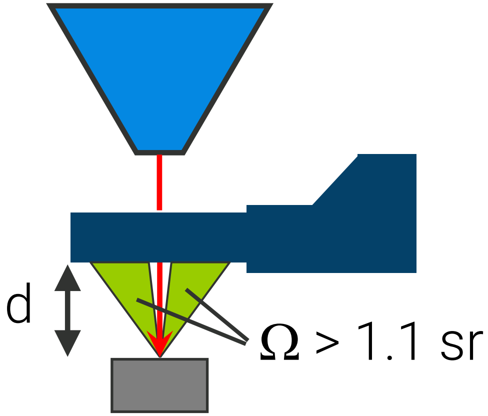




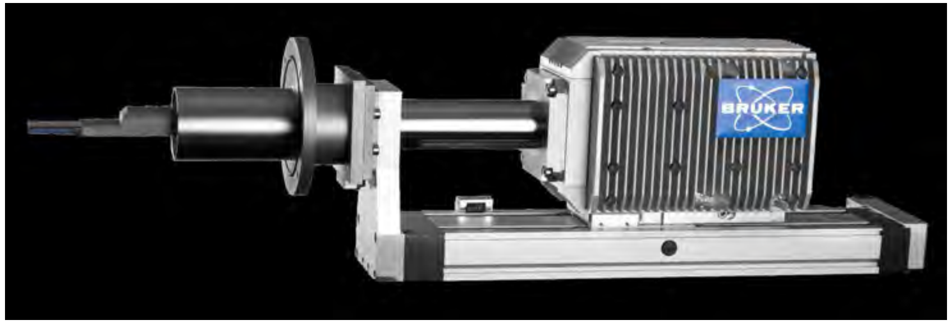


Bohr´s atomic-model

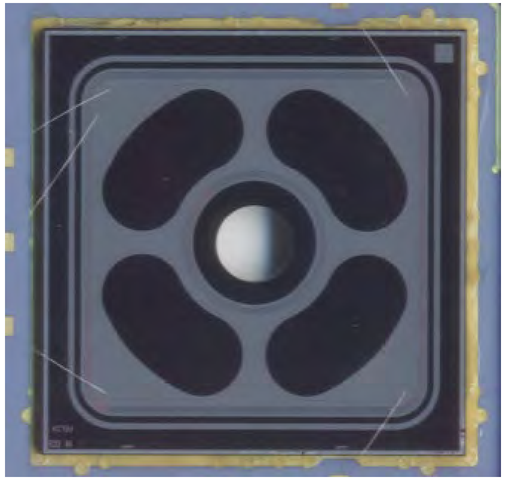
Advantage of high take-off angle and annular design **XFlash® Flatquad**



- Annular design, 4x15 mm²= 60 mm²
- Placed between pole piece and sample (hole in the center for the primary beam)
- Energy resolution Mn Ka ≤ 129 eV
- Combination of high count-rate capability and high solid angle (W ~ 1.1 sr)



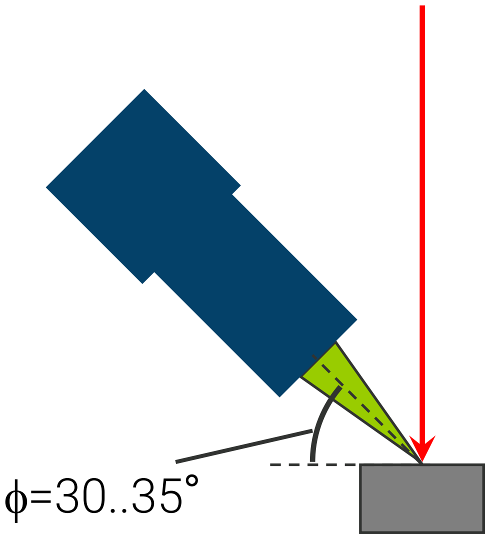
Internal SEM view



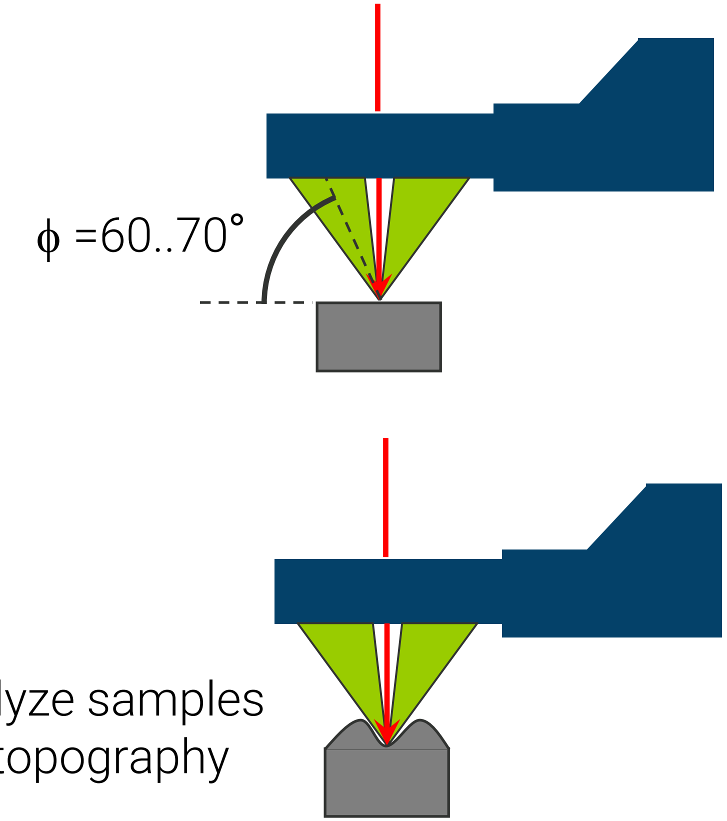
Annular detector arrangement

Advantage of high take-off angle and annular design
XFlash® Flatquad

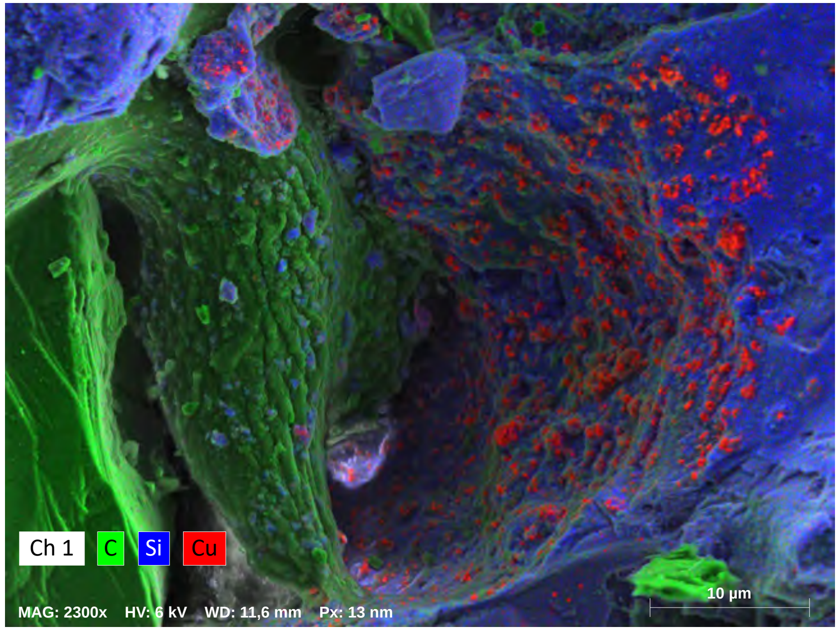
Conventional SDD



XFlash® FlatQUAD

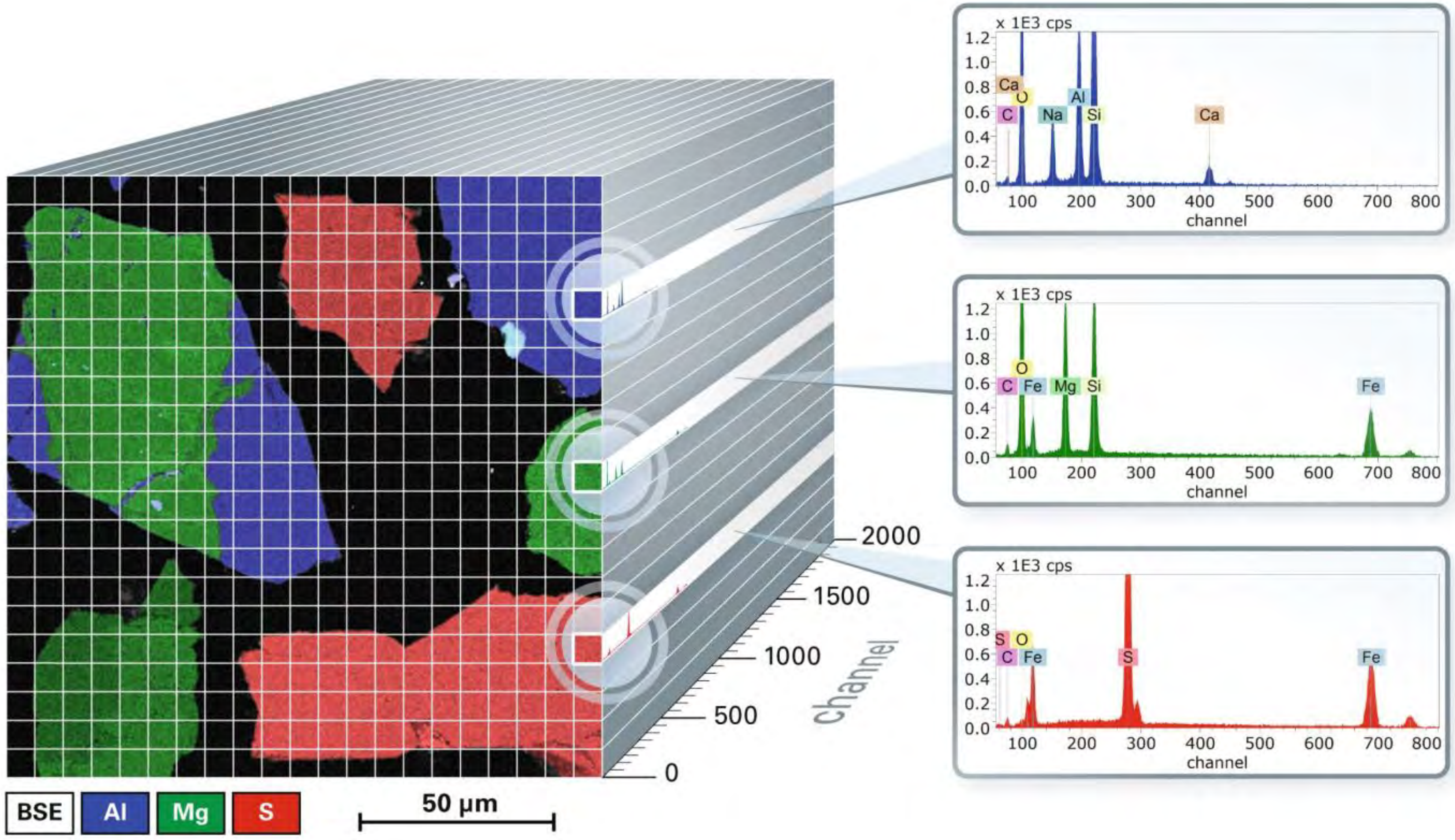


Note ability to analyze samples with changes in topography



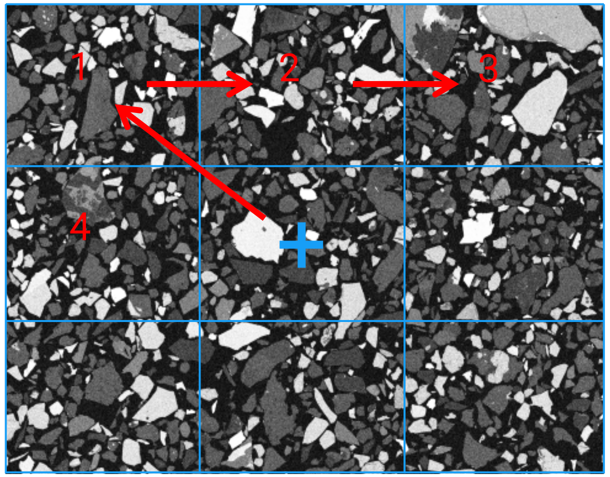
Elemental map overlying a secondary electron image showing distribution of mineral components

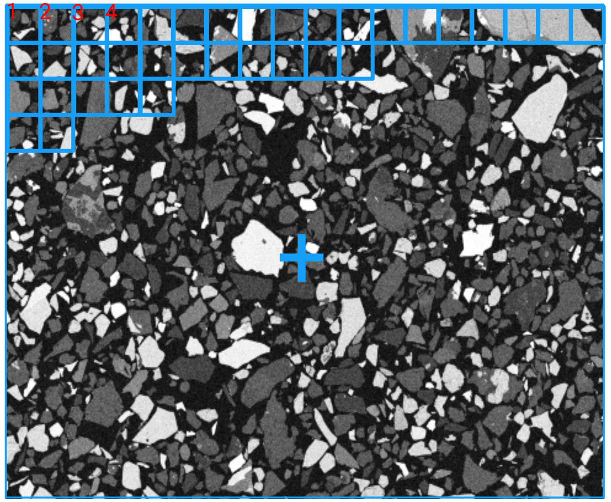
Not just an image but a data cube **Hypermap**



- A spectrum is saved for every pixel in the element map
- This data is accessible at any time after the map is completed
- Enables on- and offline processing
- Live background removal and deconvolution
- Fast quantification of pixels across the entire map (Qmap)

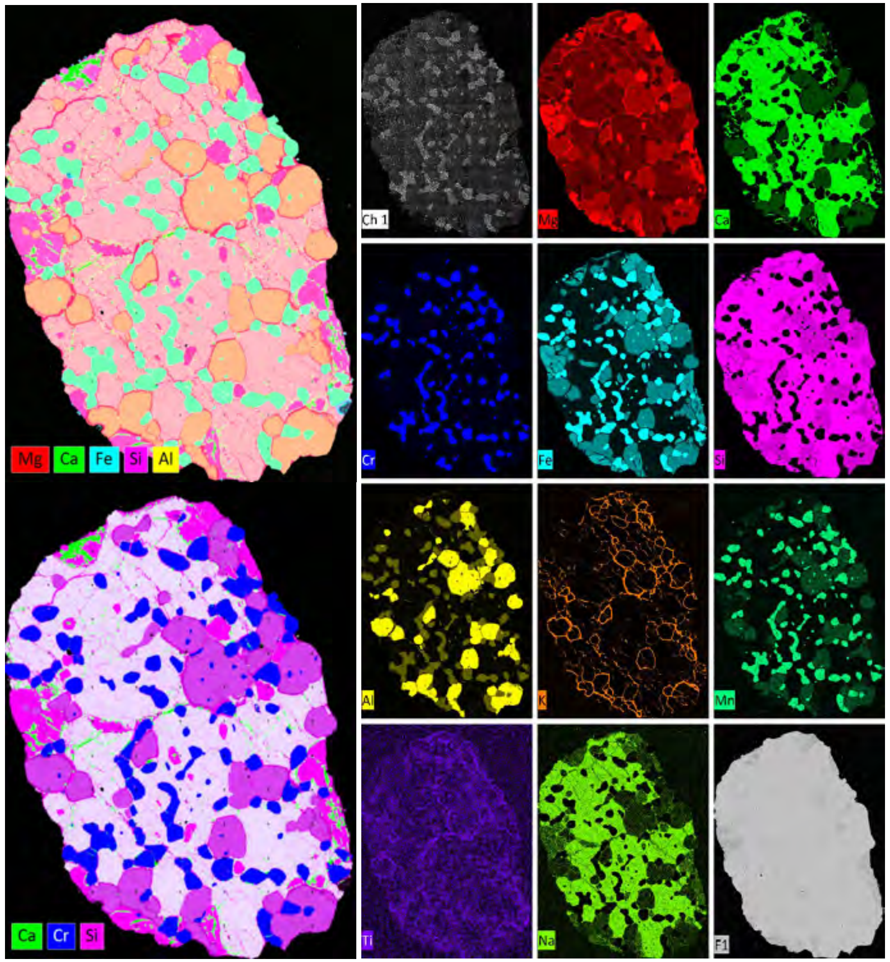
Collecting large area Hypermaps
Image extension





- From a central stage position the number of x/y frames can be defined to complete a map at any magnification
- Result: fields are stitched to form one Hypermap file
- Image extension for a full sample map with more than 20,000 x 15,000 pixels

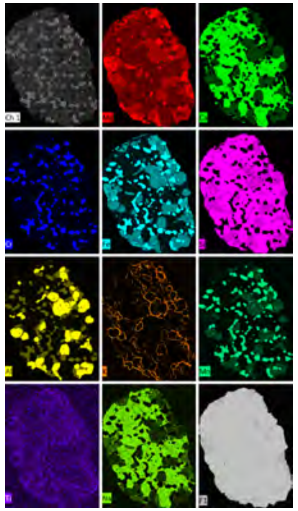
Stitched single or mixed element intensity maps



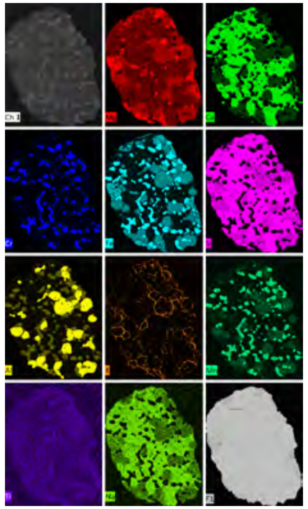
HV: 15 kV
Pixels: 800 x 1050
Time: 28 min
Dwell time: 2048 µs
FOV: 16 mm
Pixel size: 15 µm
Fields: 8 x 14 (112)
Magnification: 200x

Collecting large area Hypermaps
Rapid map collection using FlatQUAD®

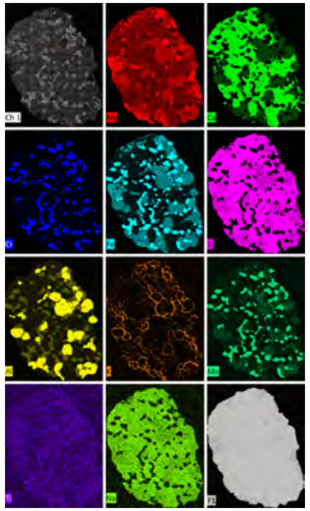
800 px
512 dw
462 min



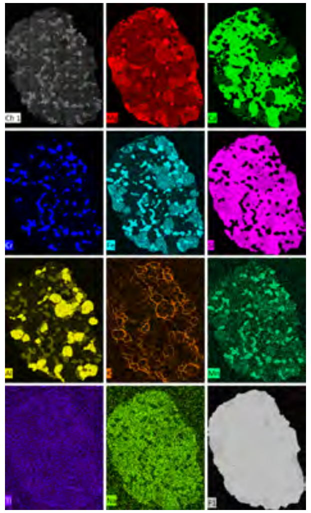
100 px,
2048 dw,
28 min



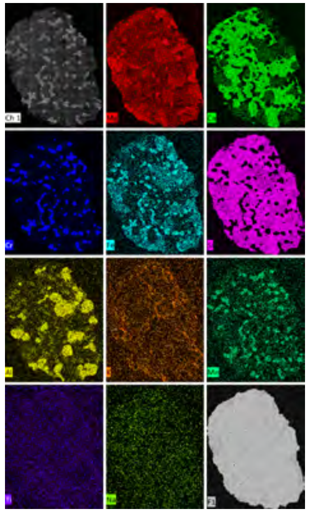
100 px,
256 dw,
4 min



100 px,
32 dw,
26 sec

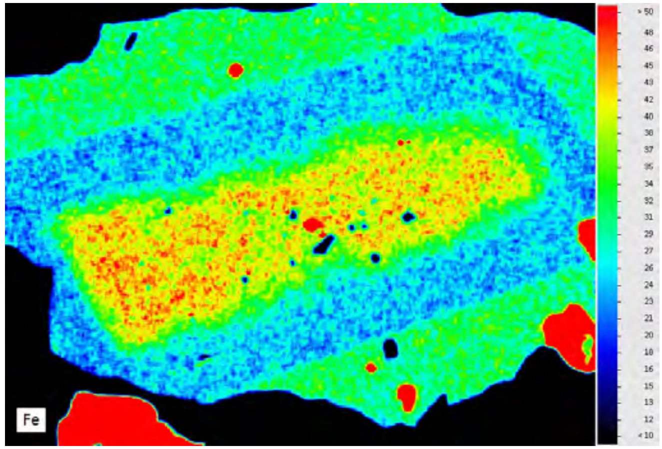


100 px,
4 dw,
3 sec

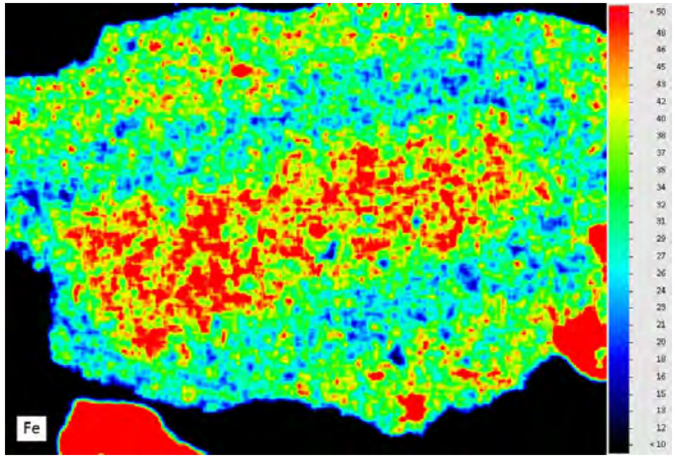


Pixel Dwell Time: Decreases

Analytical Time: Decreases



1.7 µm px, 1024 µS / px, total 256 s



1.7 µm px, 32 µS / px, total 8 s

SEM-EDS ANALYSIS IN CULTURAL HERITAGE STUDIES

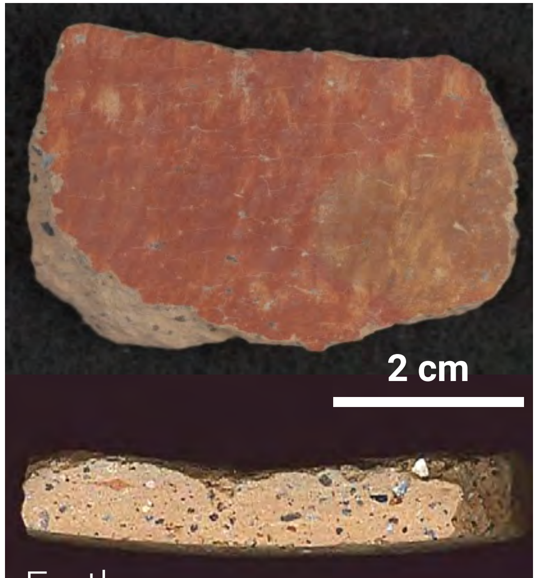
Example 1: Imaging and elemental mapping of archaeological ceramics

Archaeological Ceramics and Ceramics as Fine Art

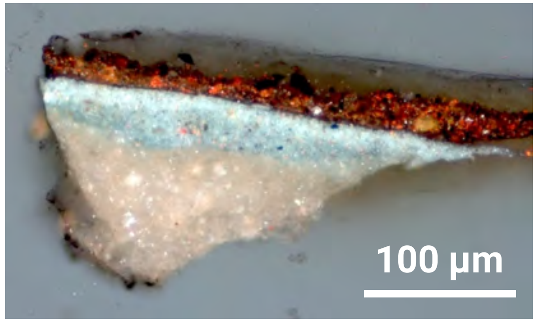
- Ceramics are very diverse and range from earthenware used for utilitarian purposes, to high art porcelains, and all areas in between

- Key questions (among many):
  - Method of manufacture
  - Origins of materials and artifacts (archaeological, historic artisans and factories, authenticity)
  - A window in other technologies & methods
  - Sourcing and dating

Chalcolithic crucible



Earthenware



Layered ceramic

Glaze & enamel on porcelain

Image credits: Prof. Aaron Shugar (Buffalo State College), Prof. Philippe Colomban (Sorbonne University)

Example 1: Archaeological ceramics
(samples courtesy of Prof. Aaron Shugar)

- Ceramics used in the process of smelting and refining metals
  - furnace walls
  - crucibles

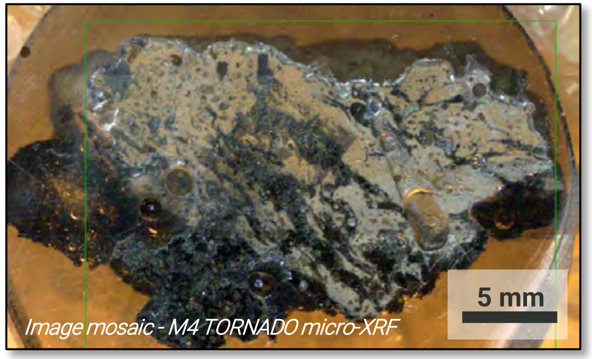
Furn walls

Crucibles

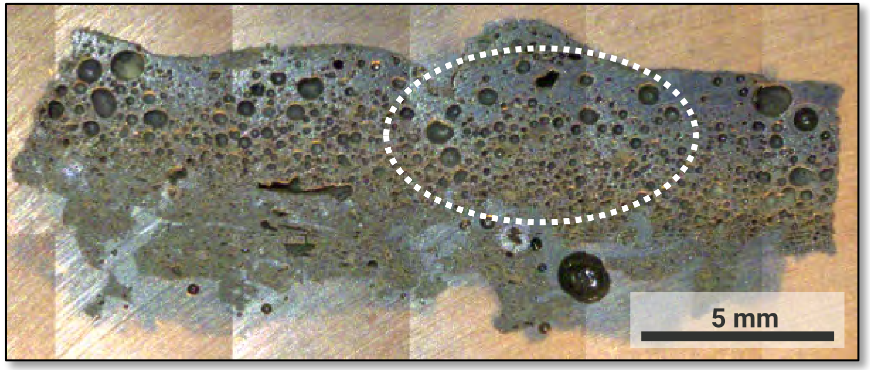
Replicating ancient smelting methods Buffalo State College

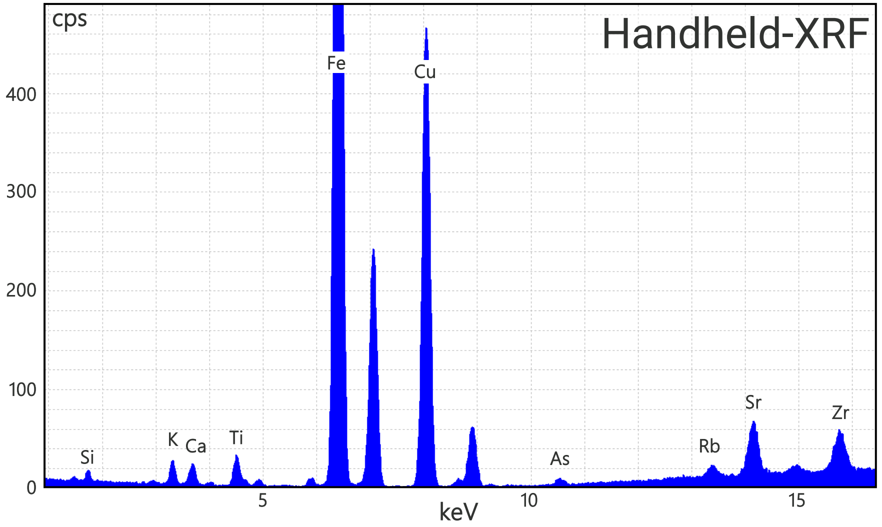
- Sample 1: Chalcolithic era copper smelting vessel (Israel)

- Sample 2: Modern iron smelting experiment (Buffalo Sate College)

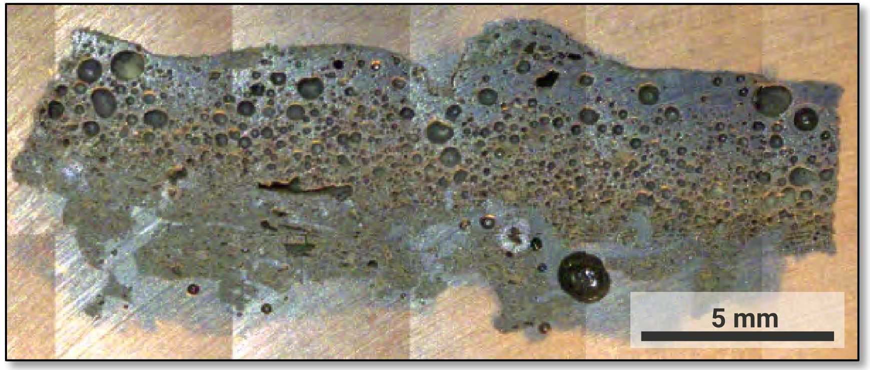


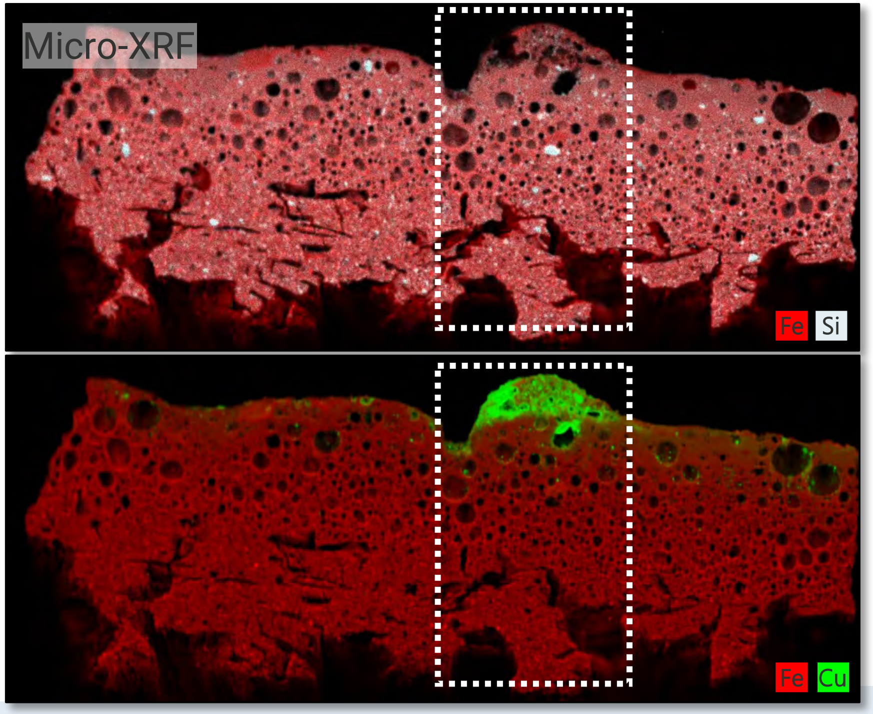
Archaeological ceramics
Chalcolithic copper smelting vessel

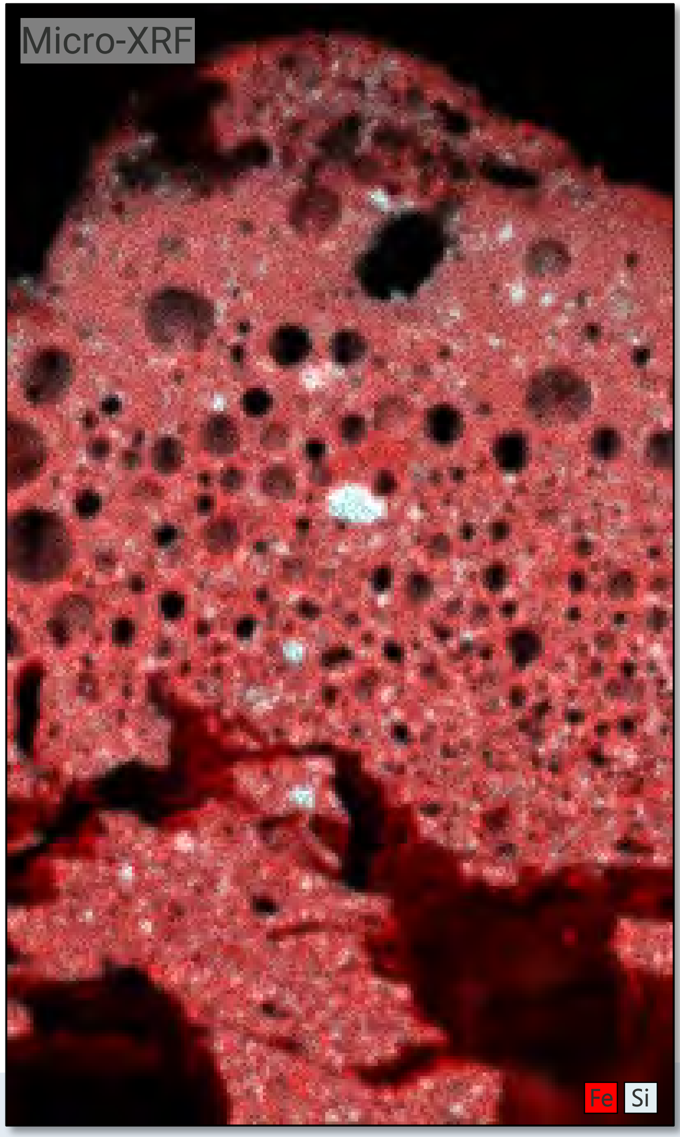


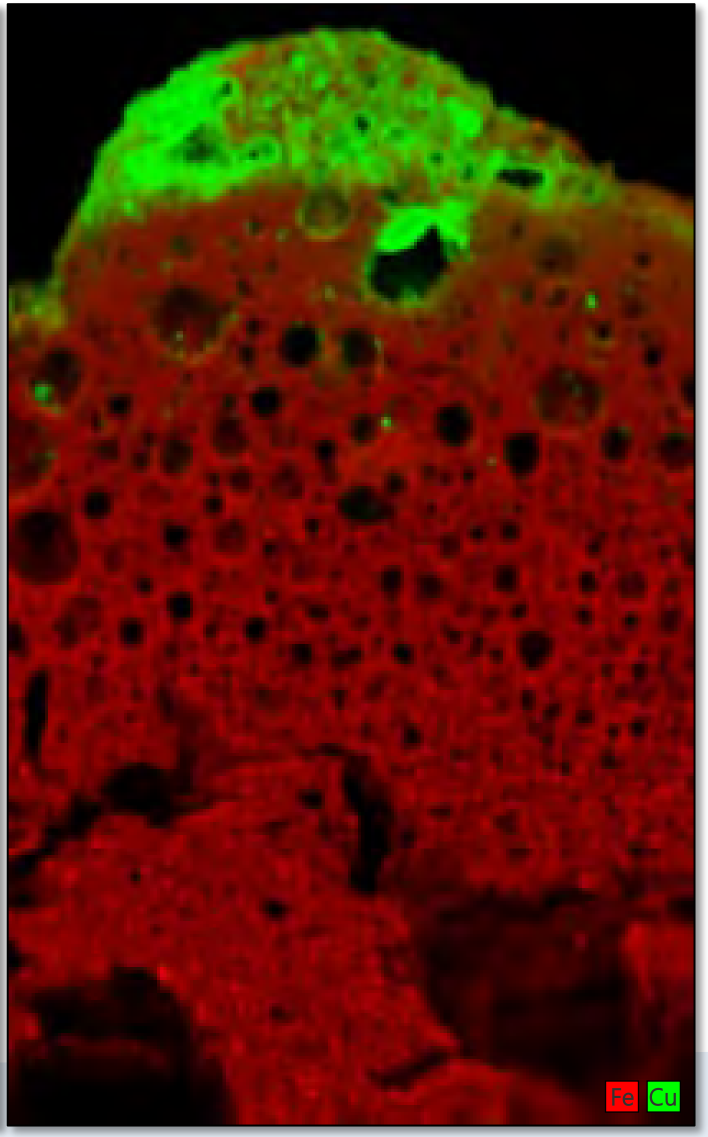


Archaeological ceramics
Chalcolithic copper smelting vessel

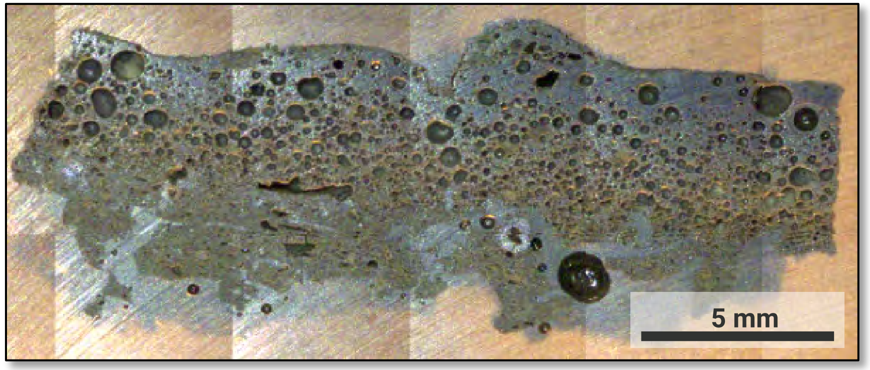


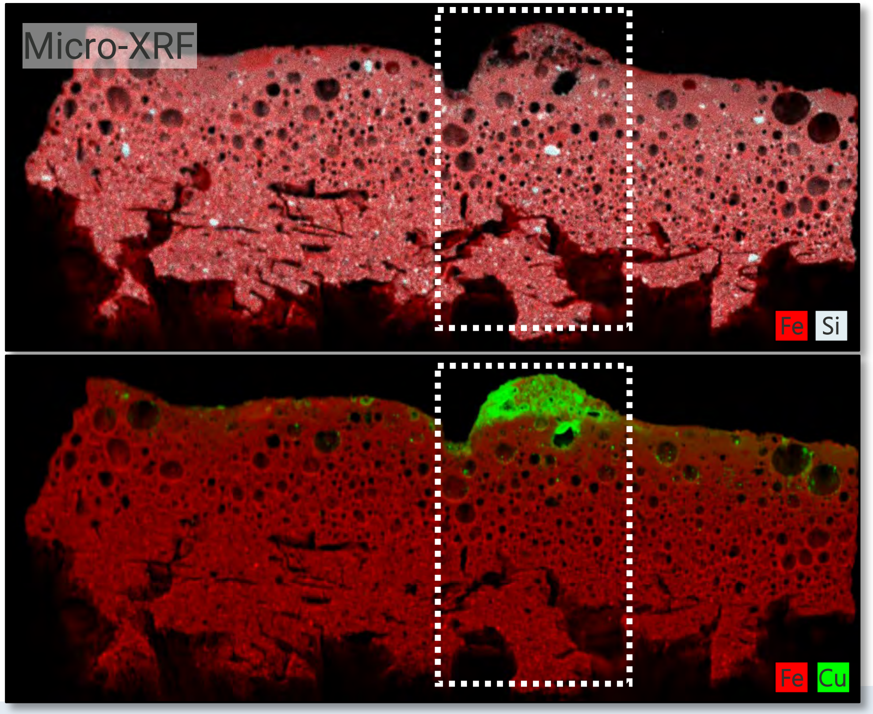


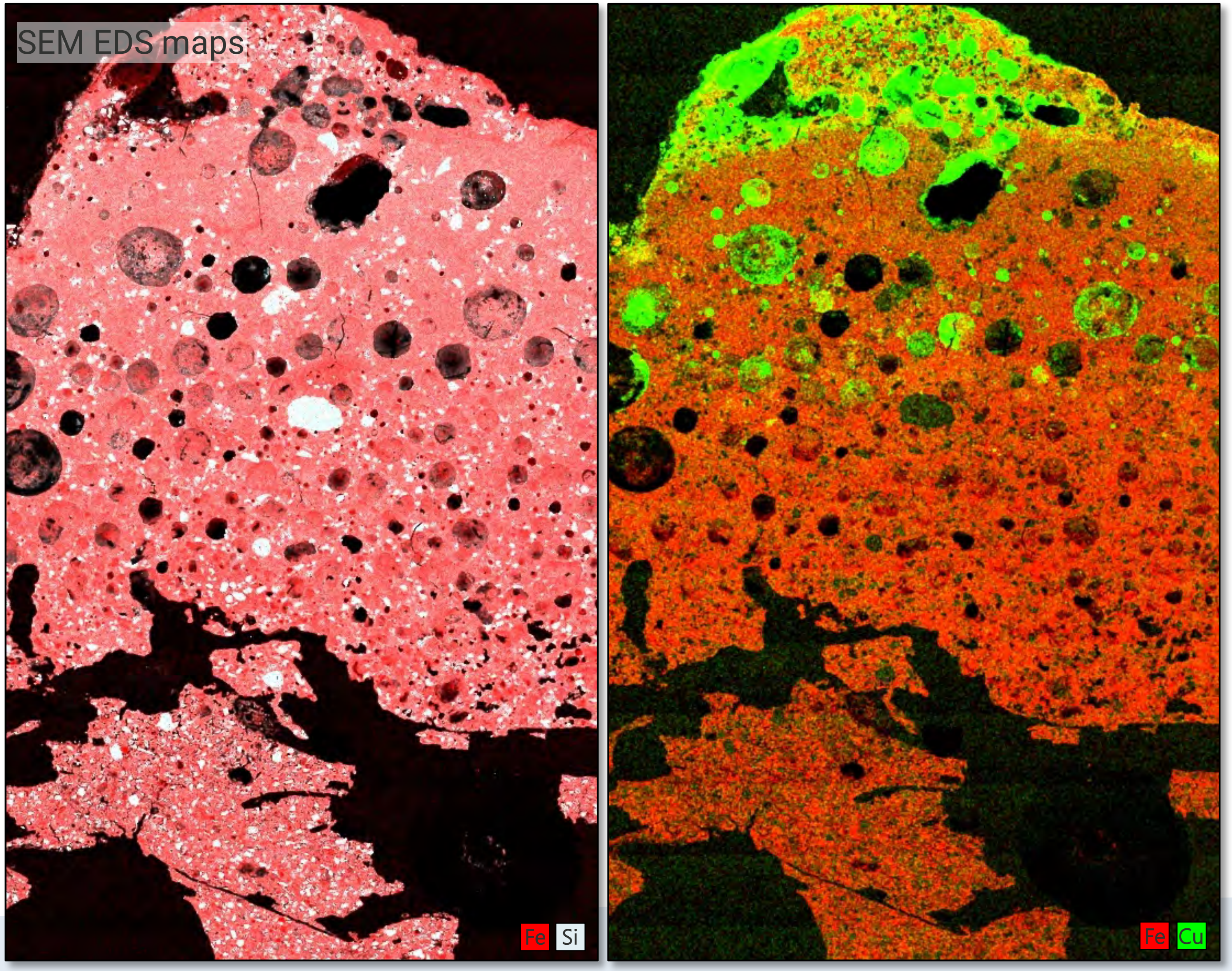




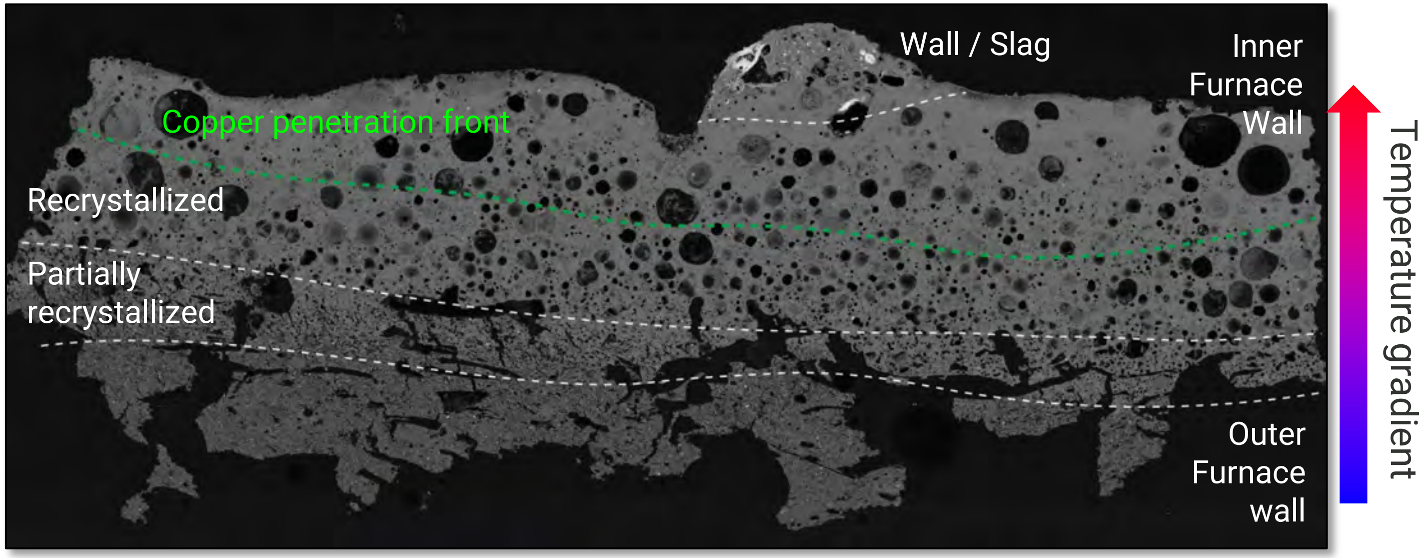
Archaeological ceramics
Chalcolithic copper smelting vessel



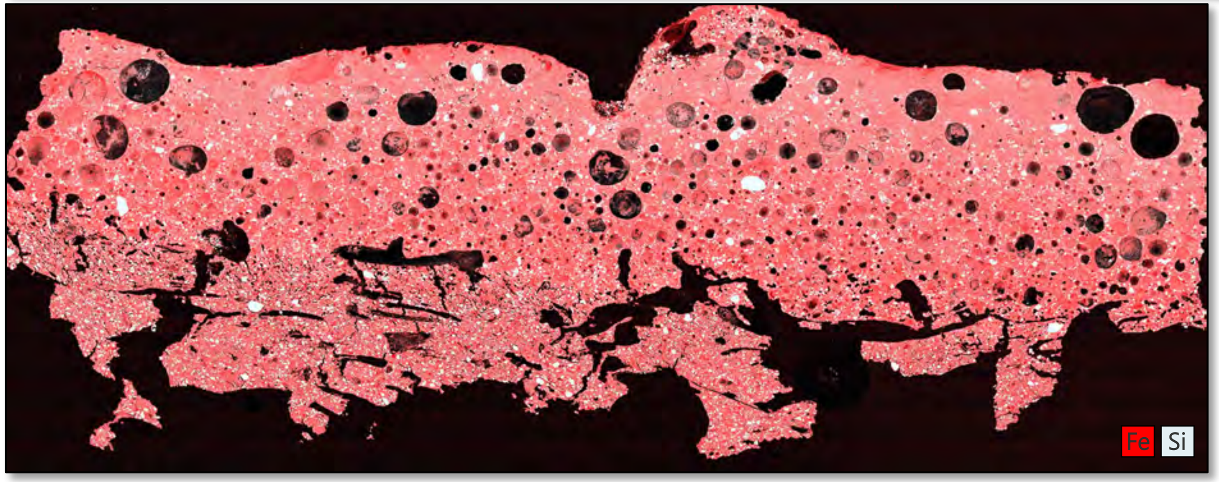


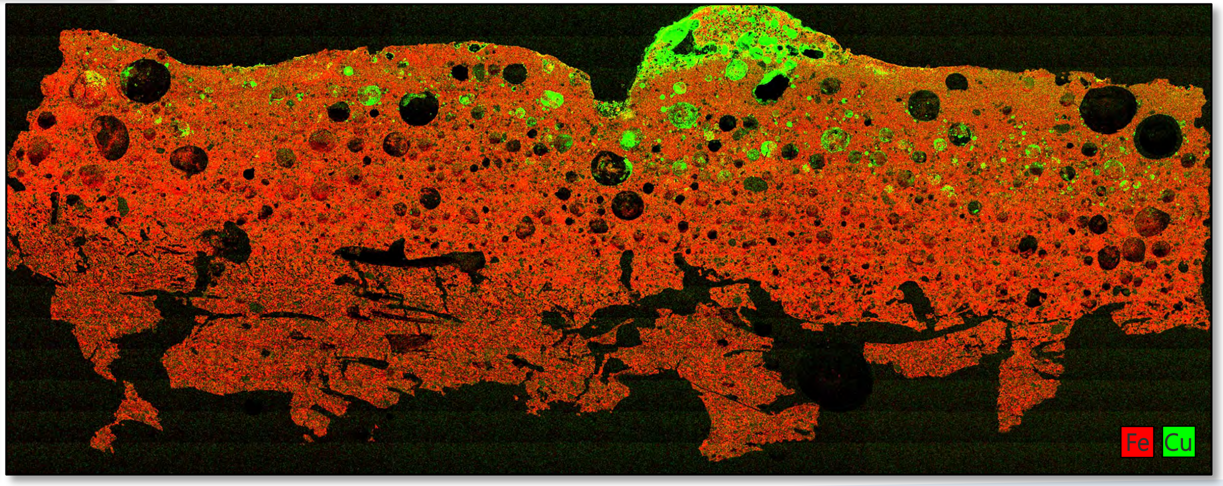


Archaeological ceramics
Chalcolithic copper smelting vessel

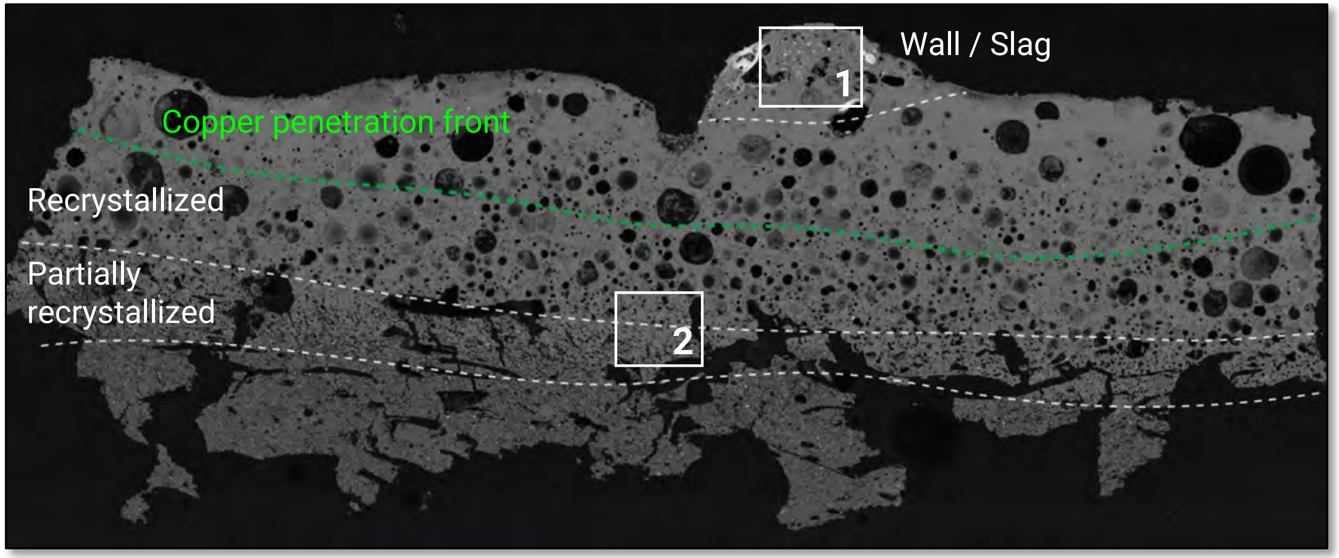


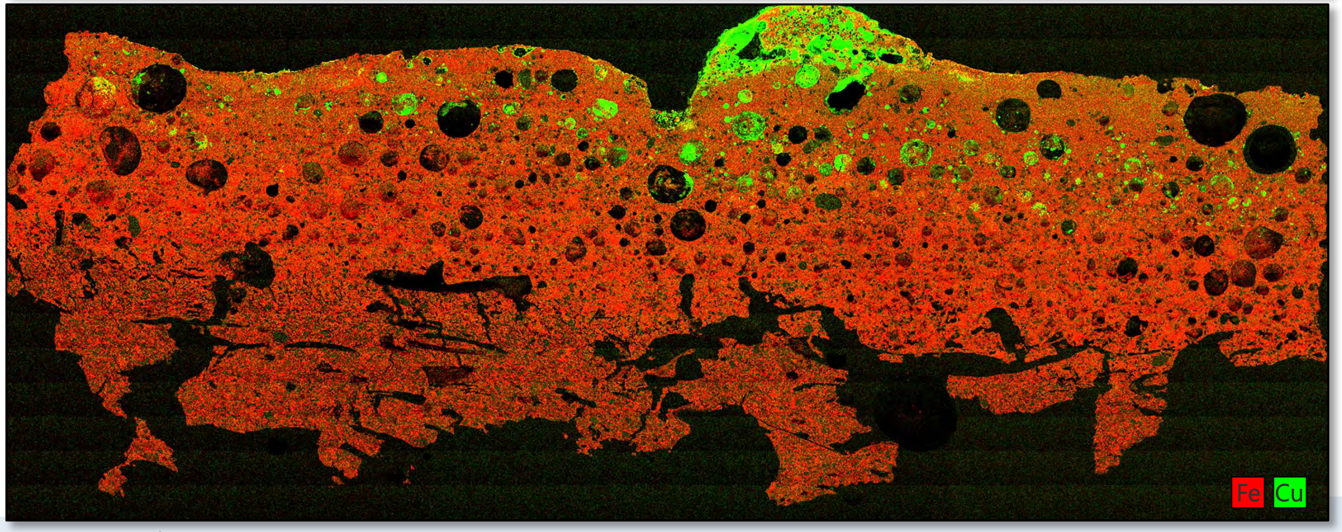
- "Image extension" whole mount EDS map of the ceramic fragment (23 x 9 mm)
  - 15 x 58 fields, 1.5 µm pixel size, 24 mins
  - Full hypermap enables data mining





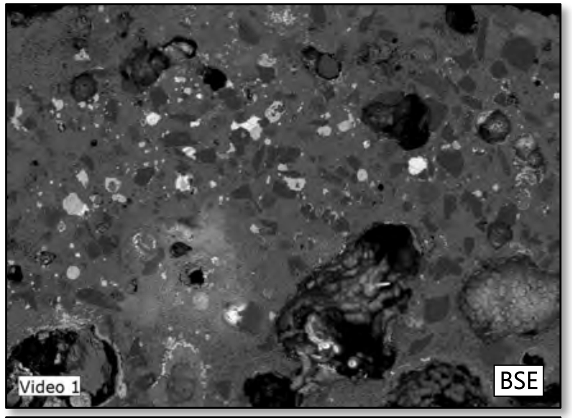
Archaeological ceramics
Chalcolithic copper smelting vessel



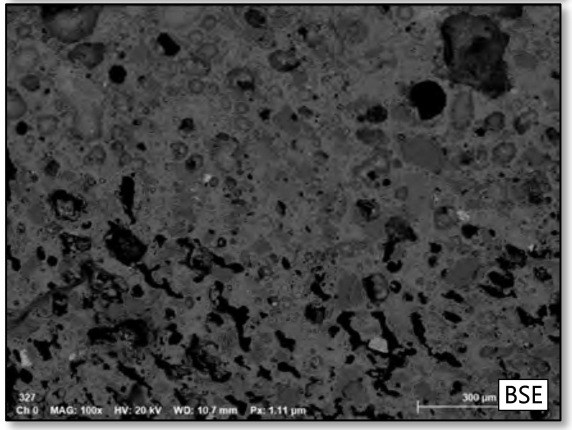


- Mapping individual fields allows even further detailed data interrogation
- 2 examples

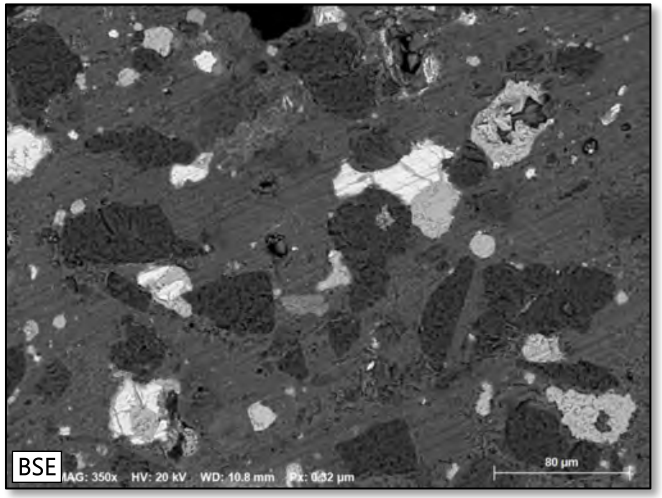
  1) Inner vessel wall, including metal remnants of the smelting process

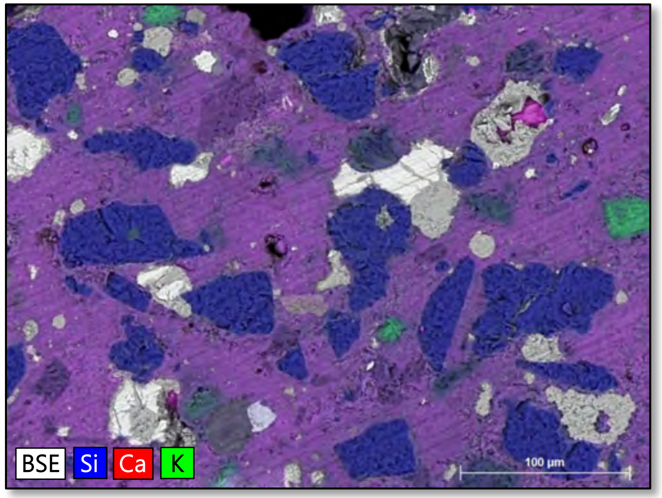


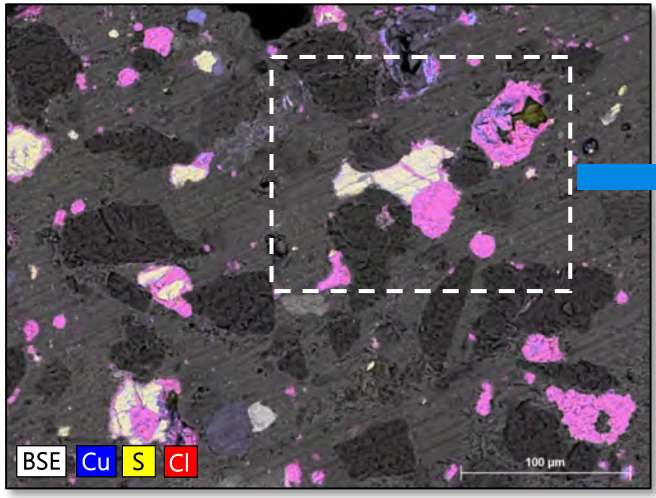
  2) Boundary between the weakly fired outer vessel wall and recrystallized inner domains

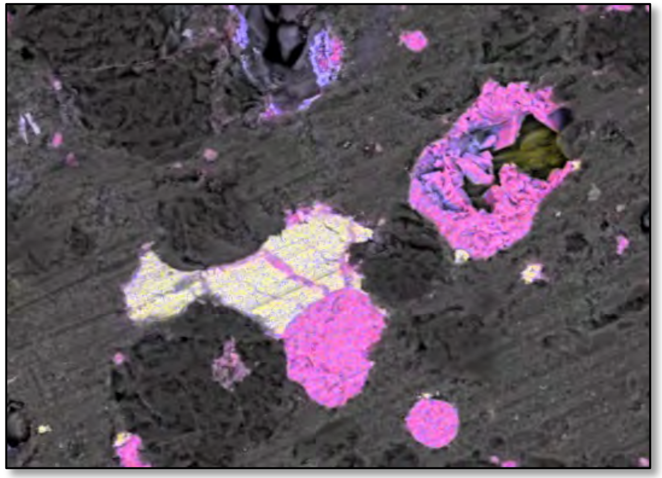


Archaeological ceramics
Chalcolithic copper smelting vessel



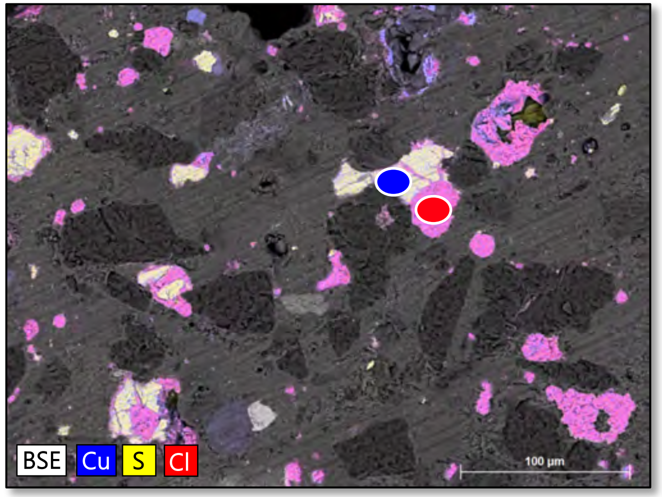


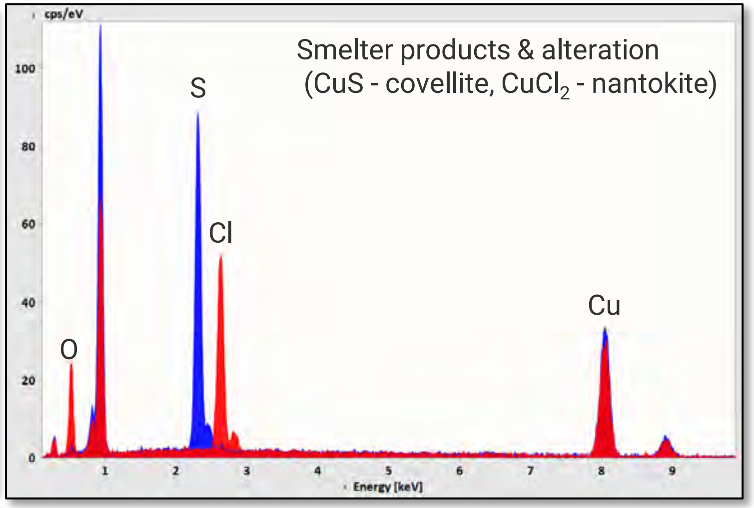


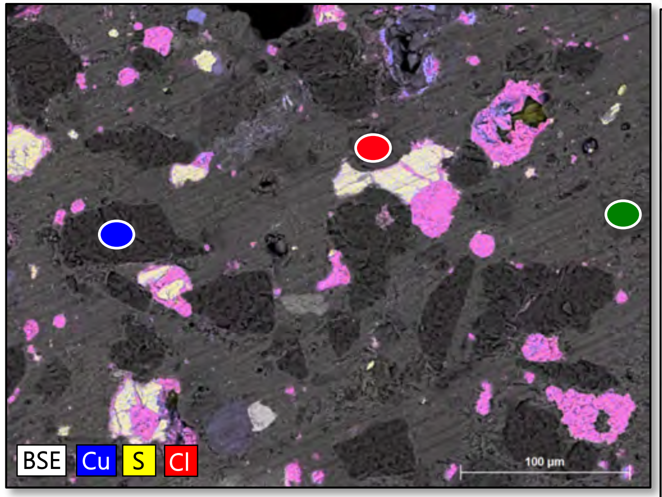


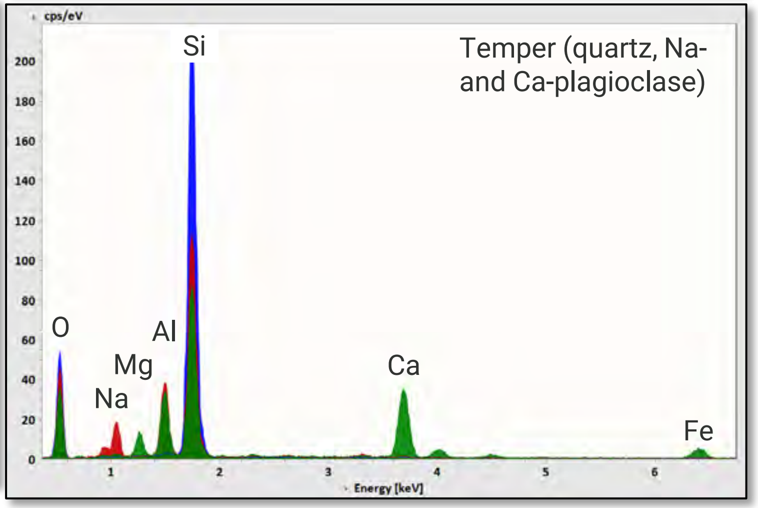
100x mag.
1327 x 968 µm²
1.1 µm pixel size
64 µs / px
10 cycles
11 min meas. time

Archaeological ceramics
Chalcolithic copper smelting vessel

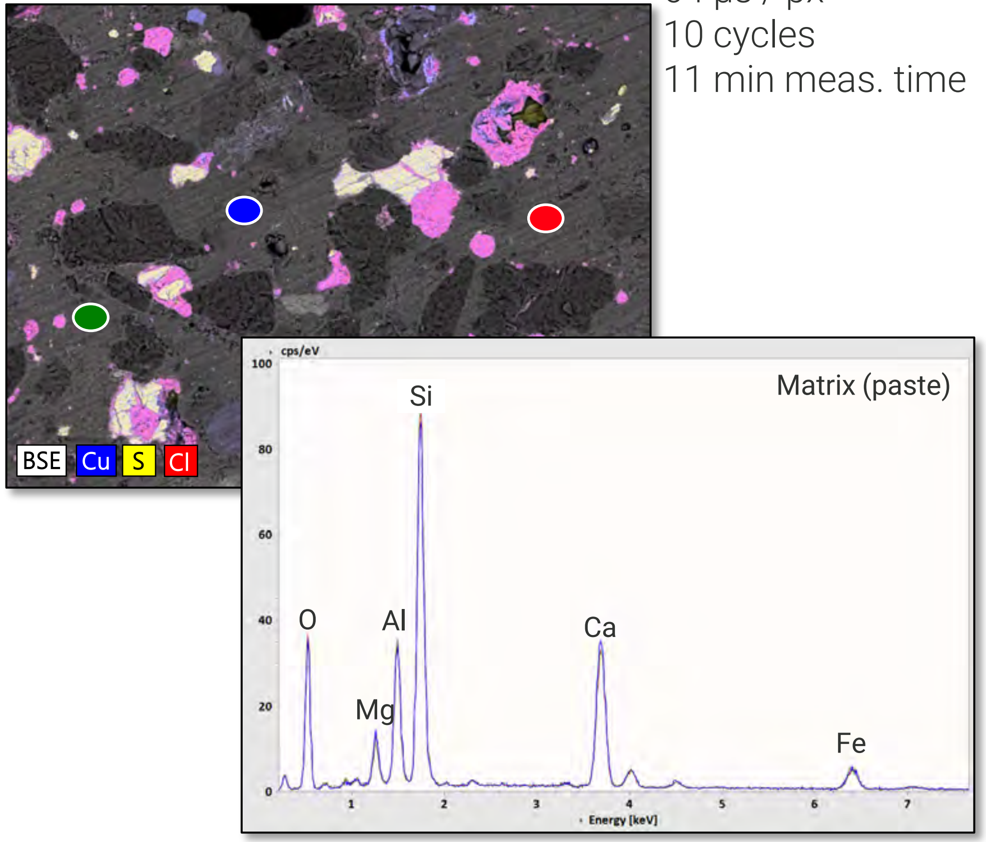




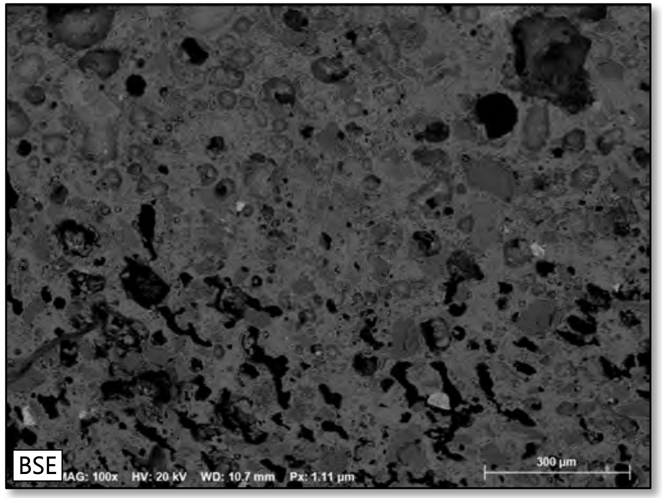


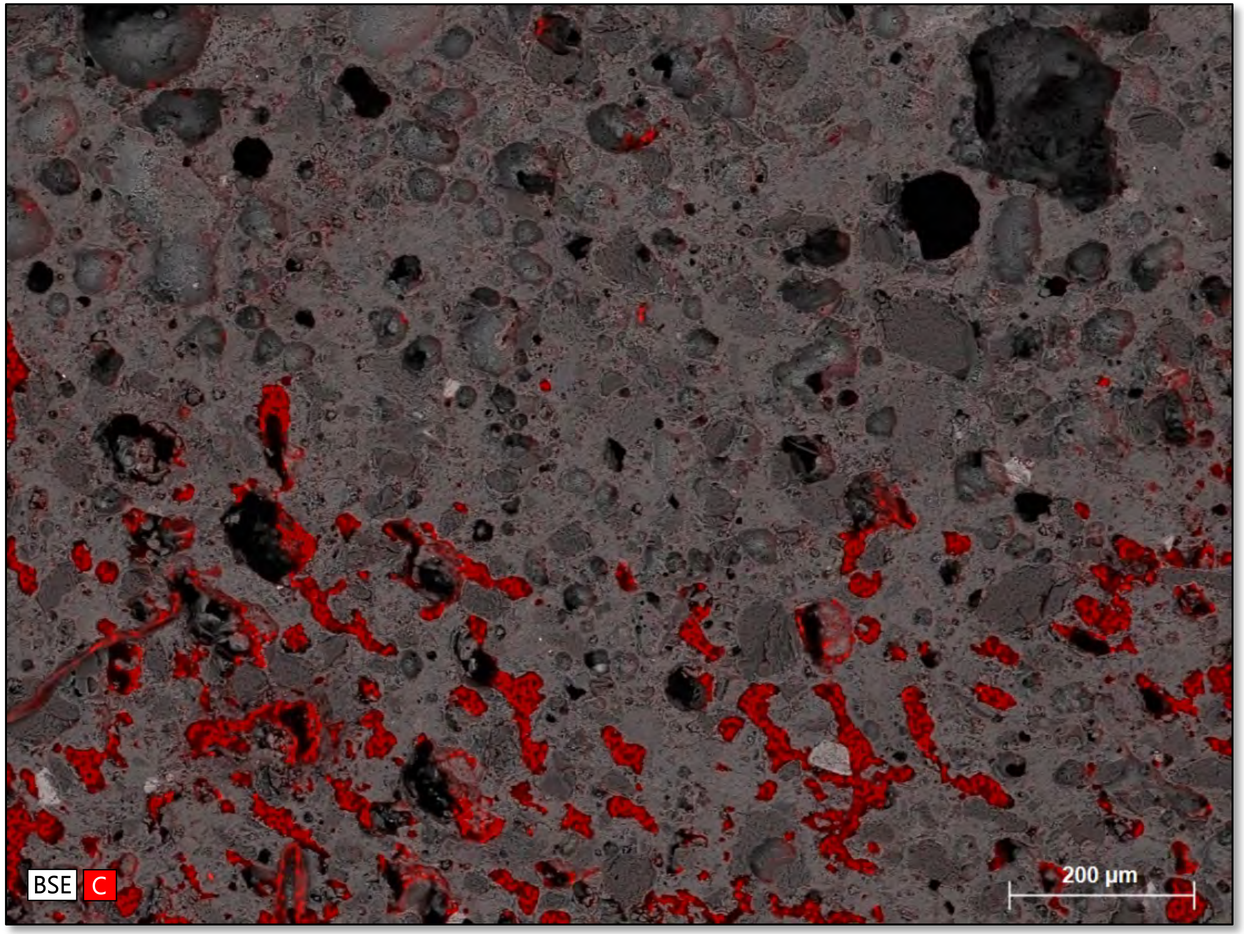


100x mag.
1327 x 968 µm^2
1.1 µm pixel size
64 µs / px
10 cycles
11 min meas. time



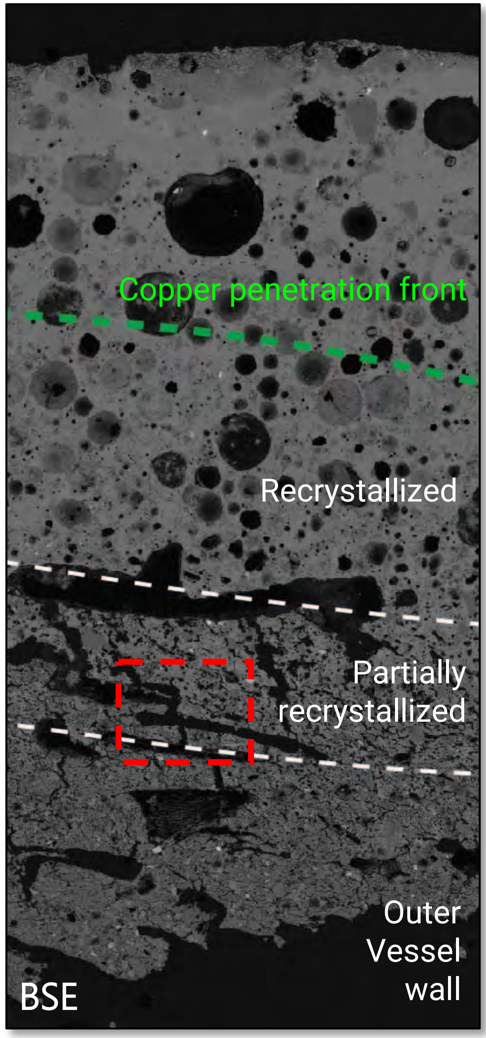
Archaeological ceramics
Chalcolithic copper smelting vessel

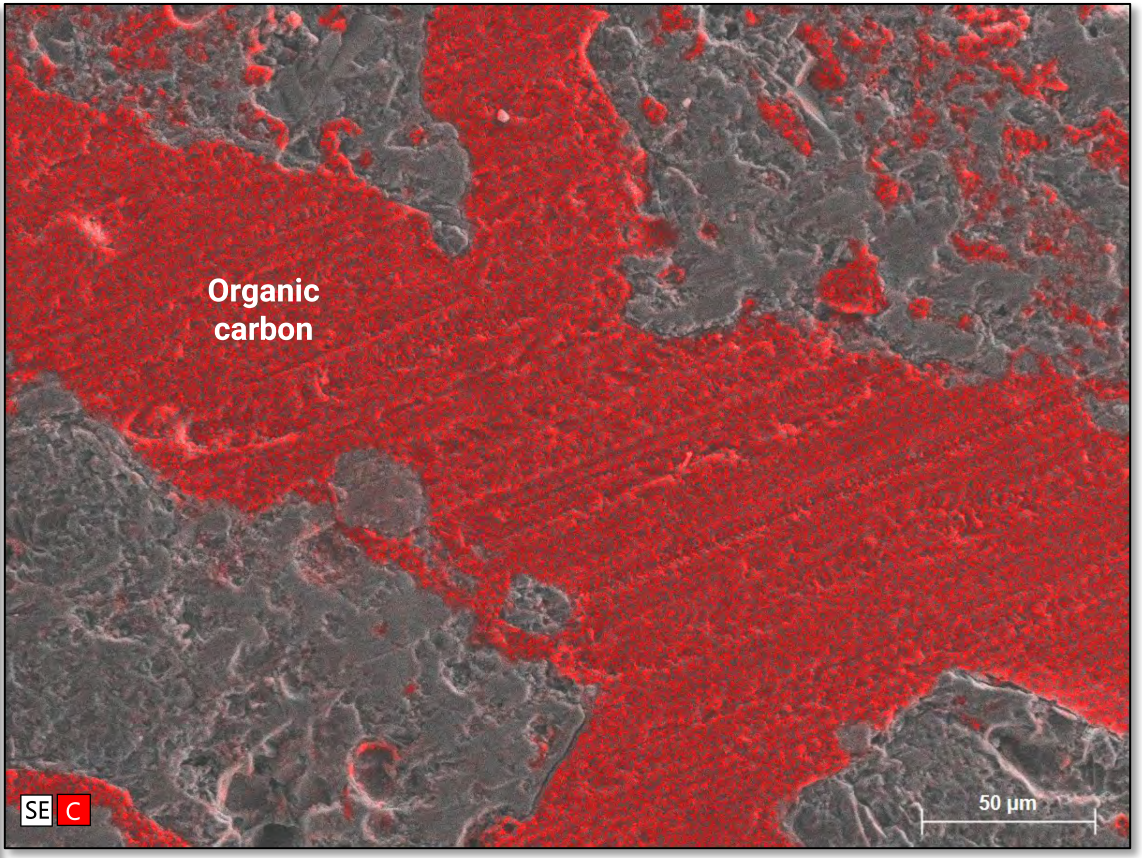




350x mag.
379 x 276 µm^2
0.3 µm pixel size
427 µs / px,
3 cycles
23 min meas. time

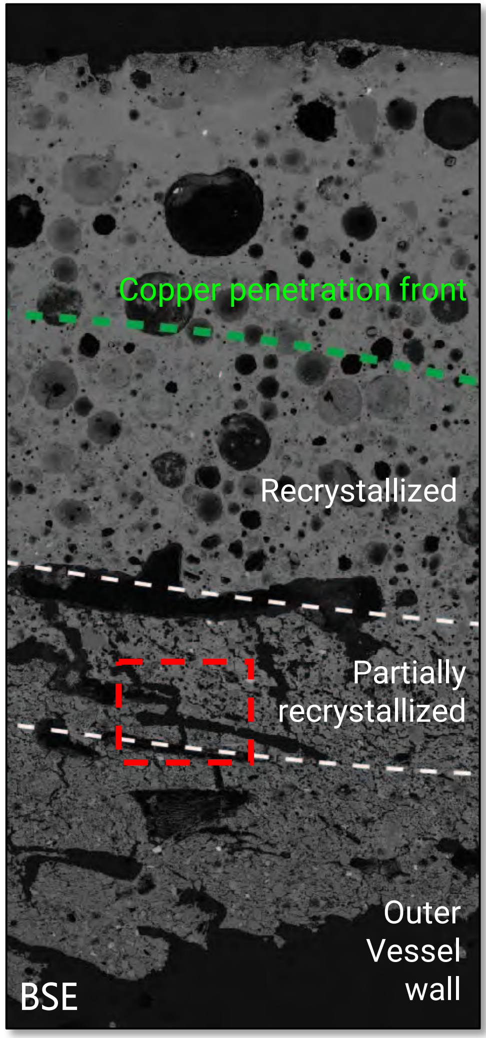
Archaeological ceramics
Chalcolithic copper smelting vessel

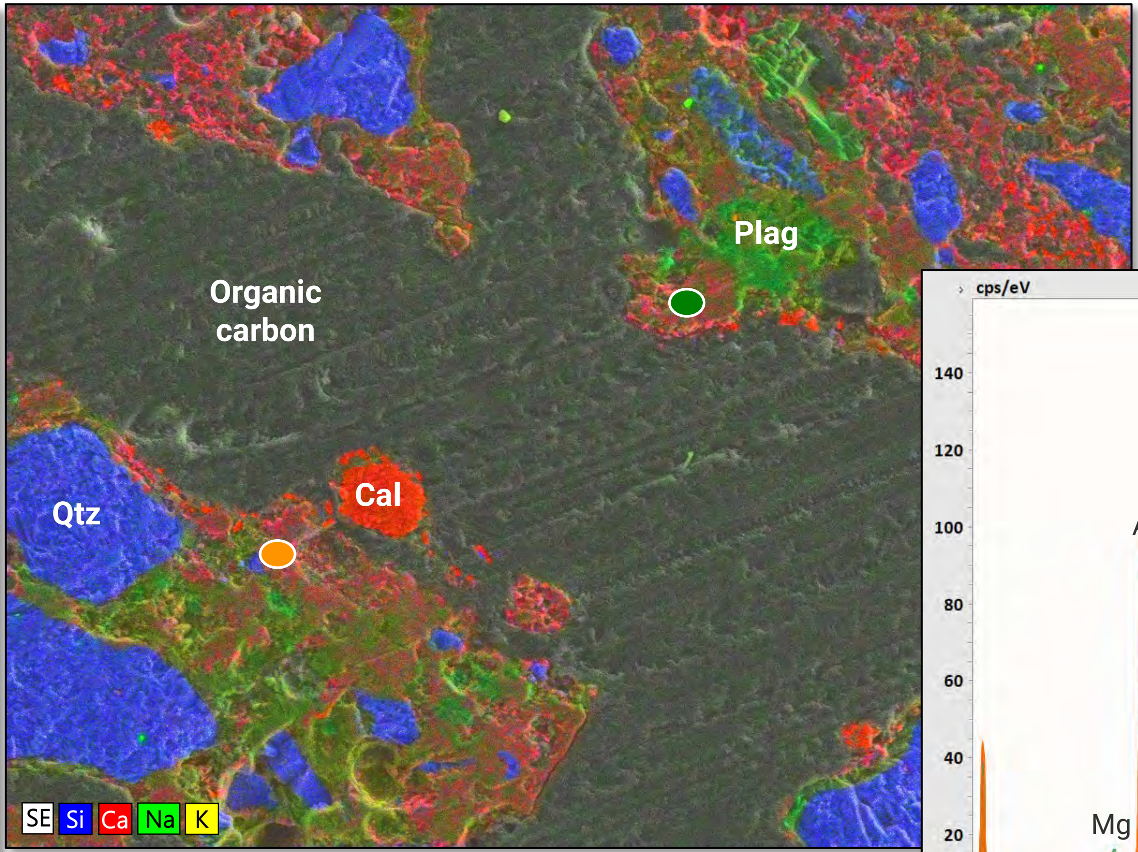


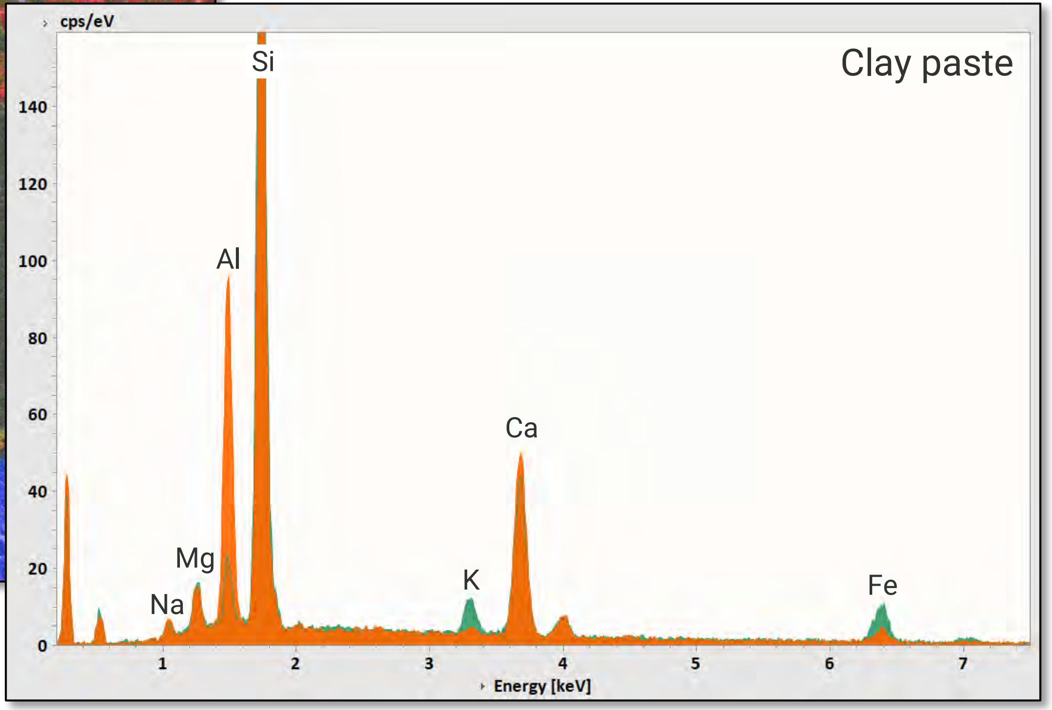


370x mag., 1200 x 900 µm^2, 0.27 µm pixel size, 13 µs / px, 44 cycles, 10 min meas. time

Archaeological ceramics
Chalcolithic copper smelting vessel

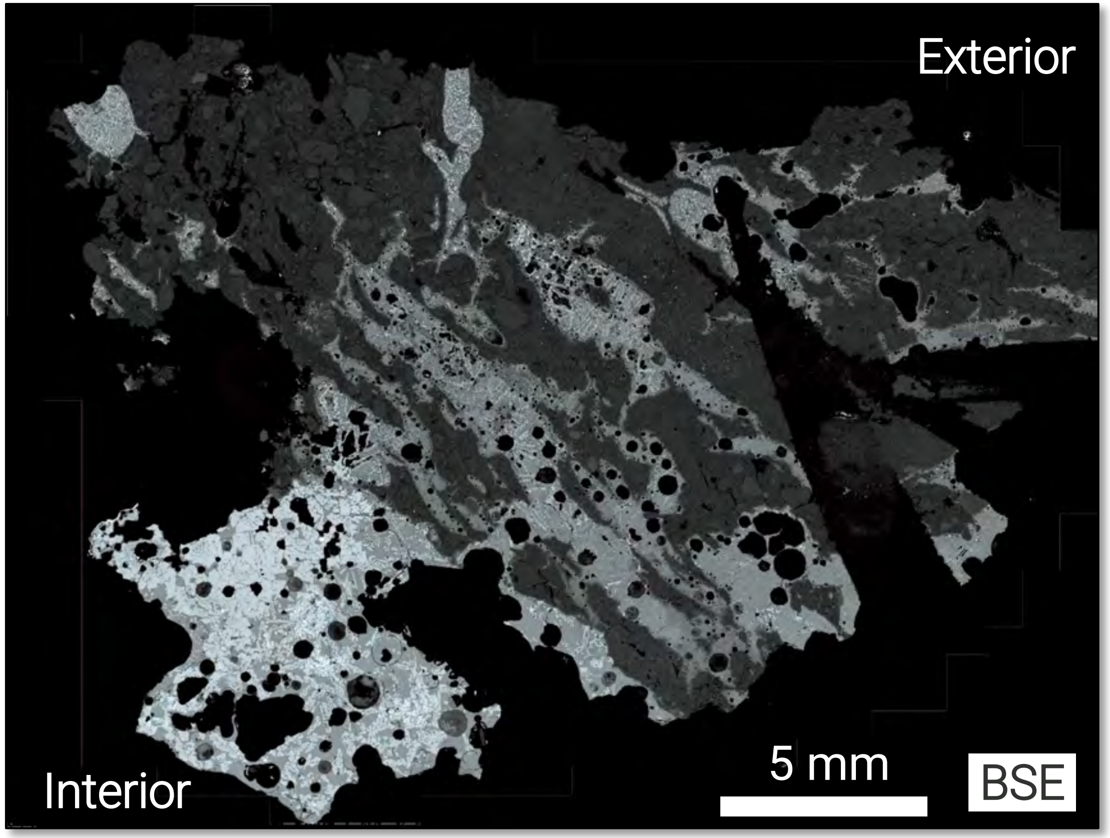


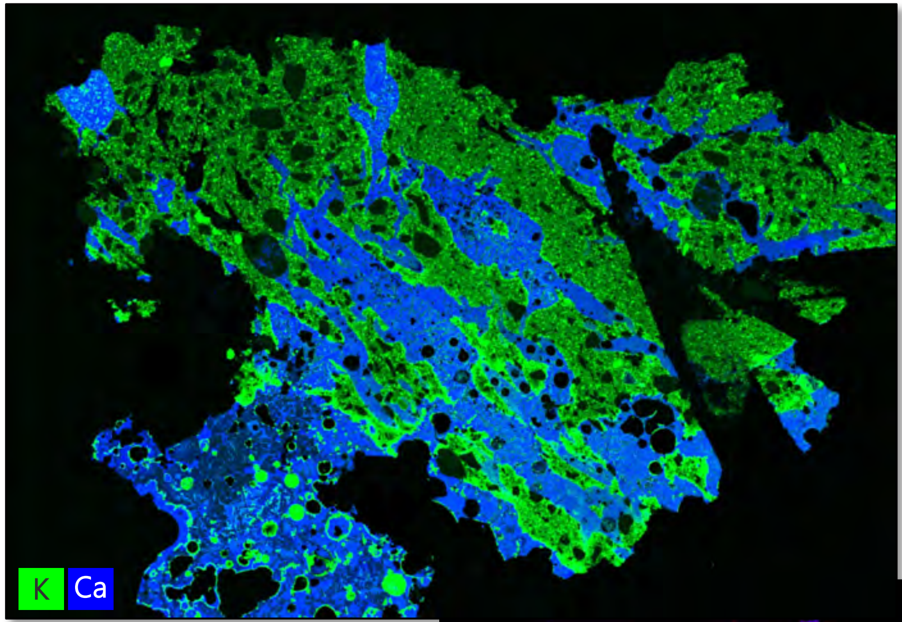


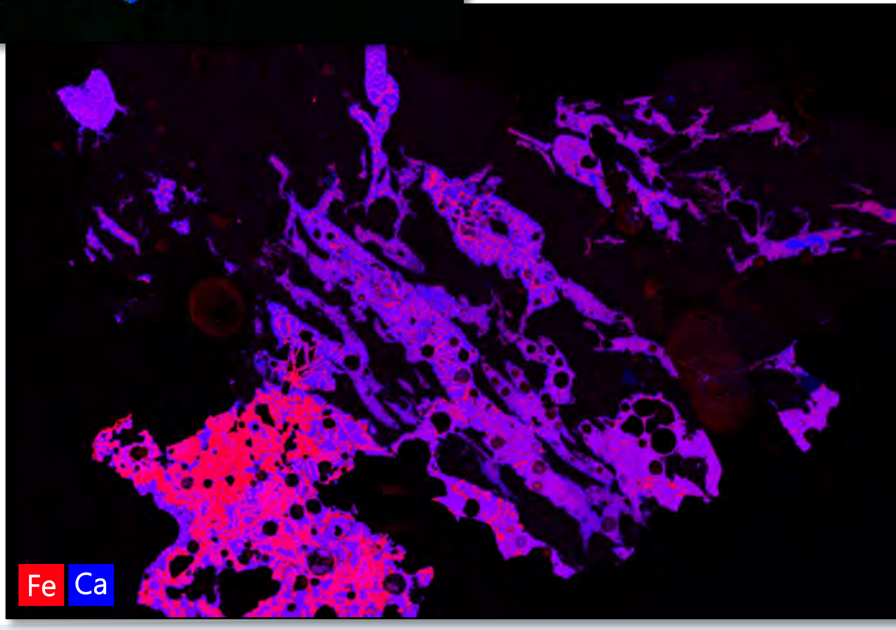


370x mag., 1200 x 900 µm^2, 0.27 µm pixel size, 13 µs / px, 44 cycles, 10 min meas. time

Archaeological ceramics
Experimental iron ore smelting vessel

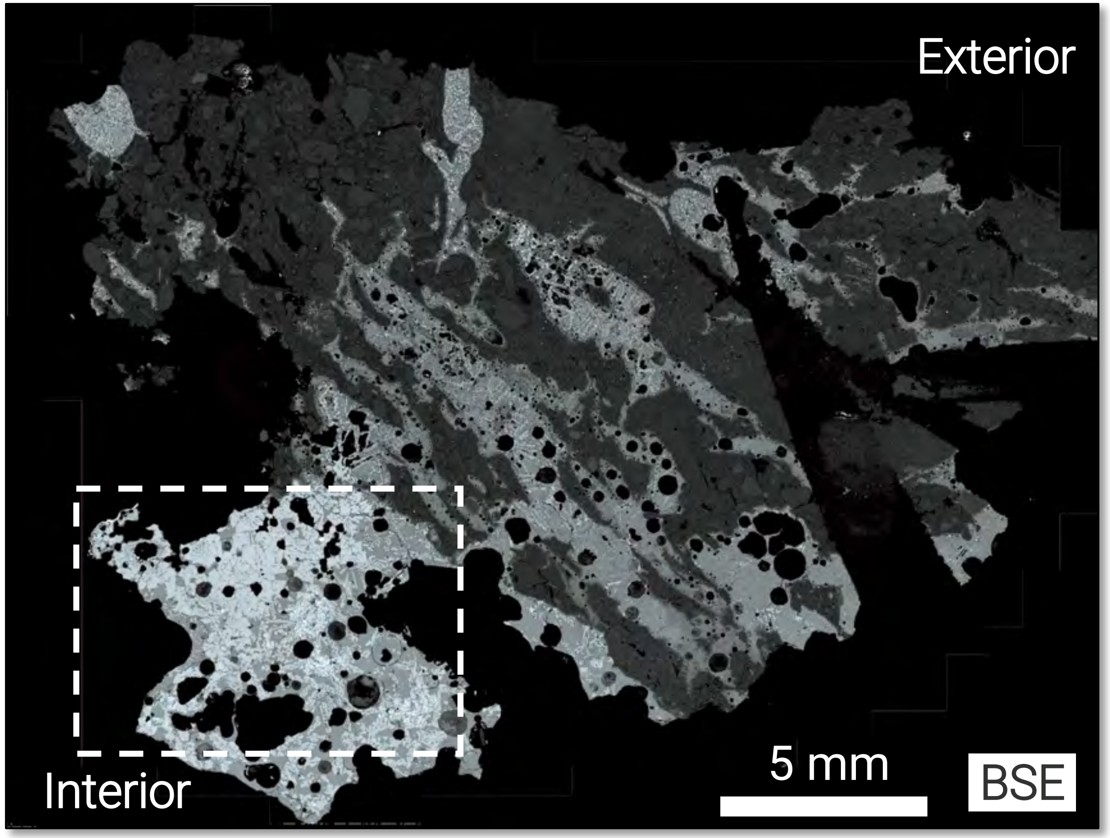


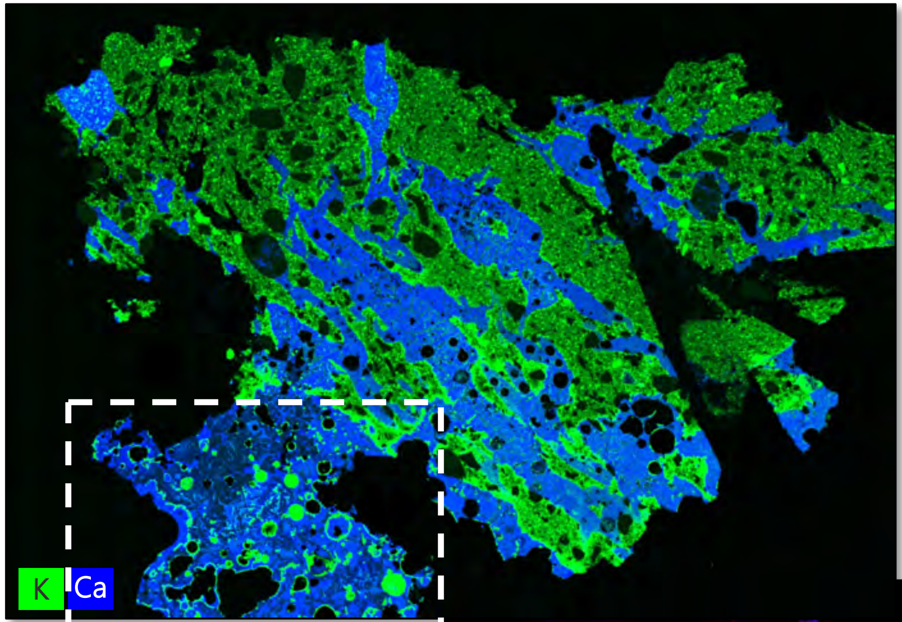


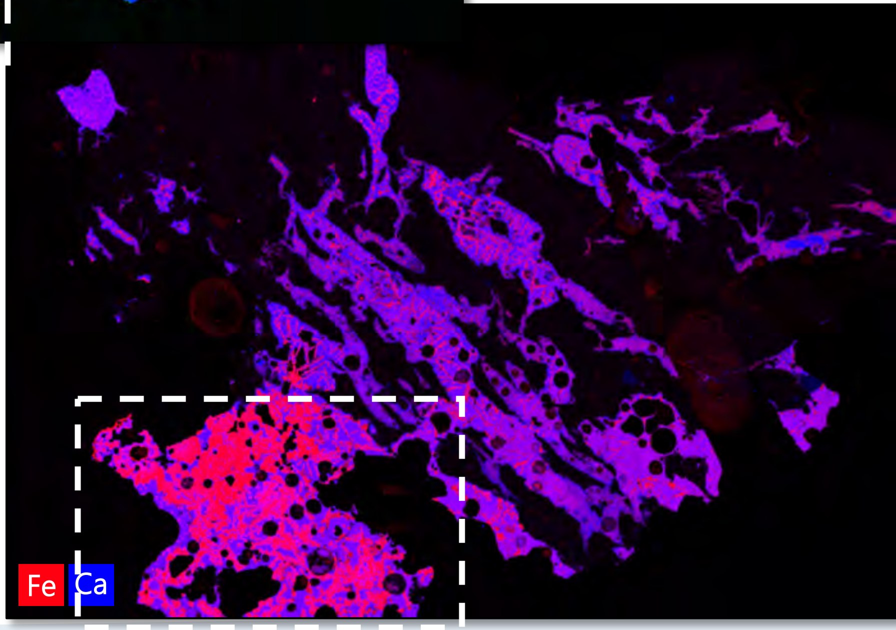


- Mosaic Backscattered Electron Image
- Image extension element maps record extraordinary detail

Archaeological ceramics
Experimental iron ore smelting vessel

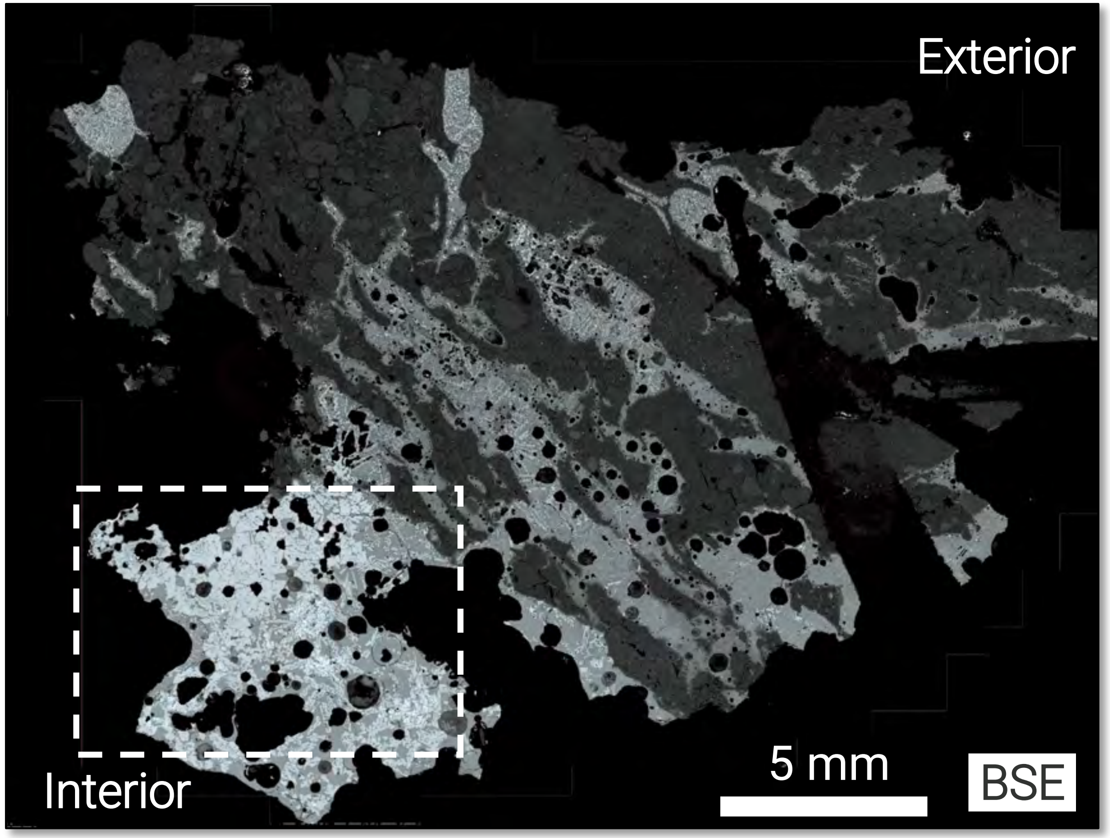


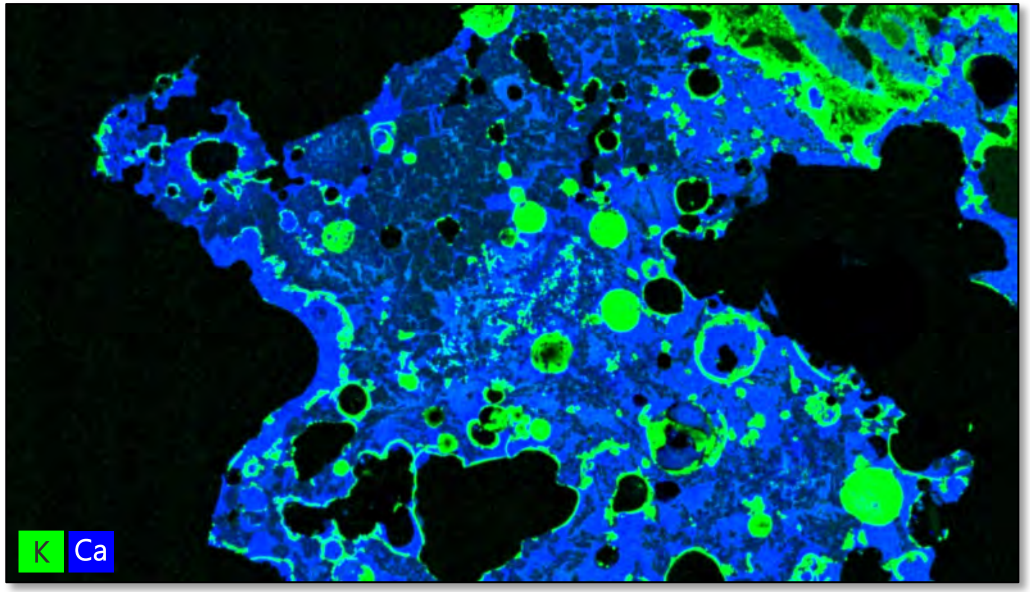


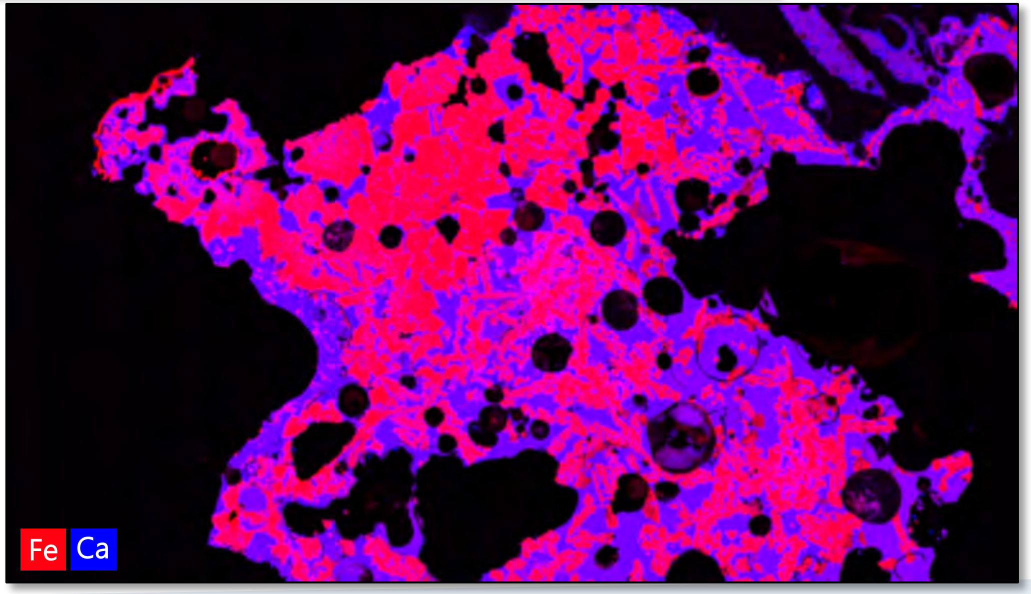


- Mosaic Backscattered Electron Image
- Image extension element maps record extraordinary detail

Archaeological ceramics
Experimental iron ore smelting vessel

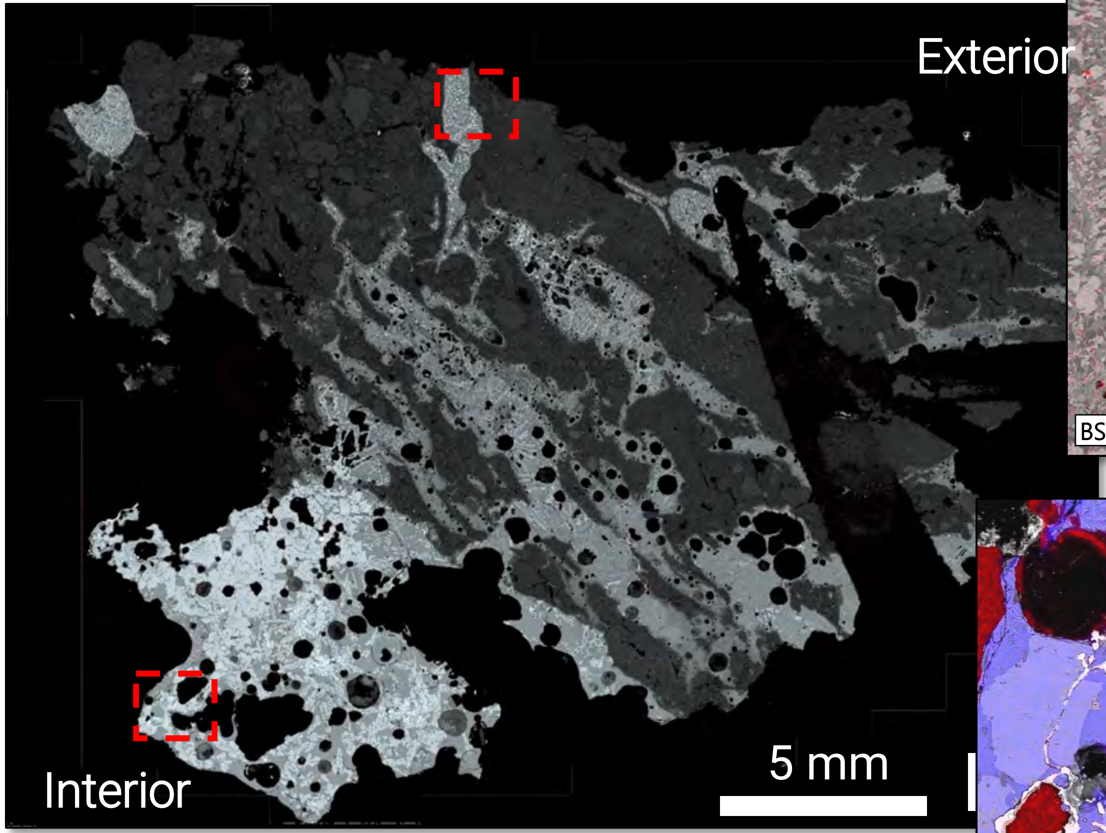






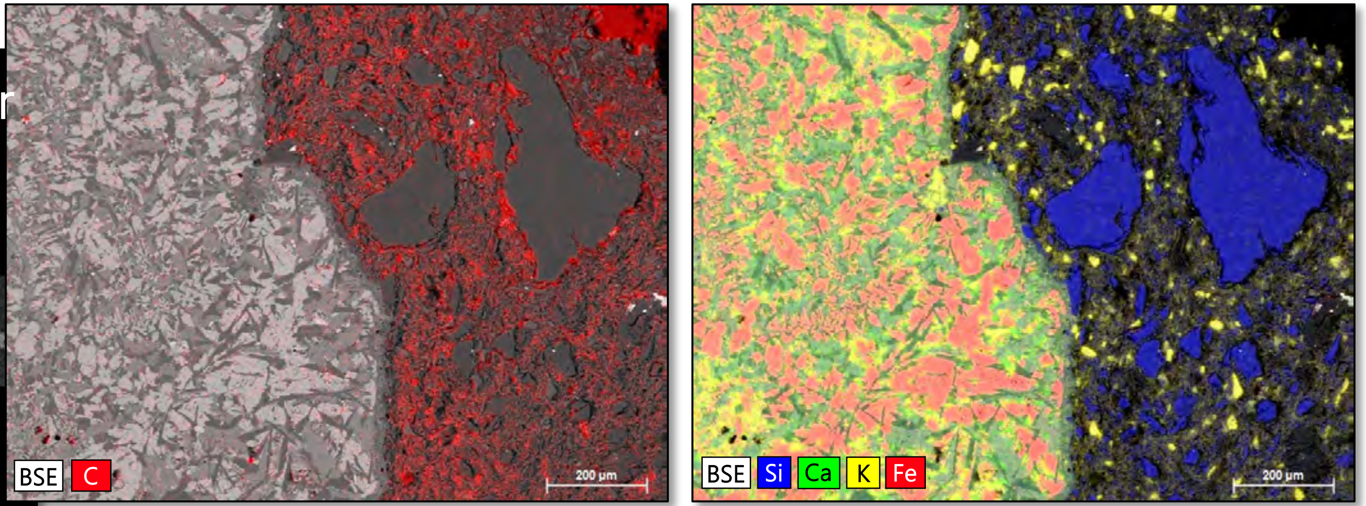
- Mosaic Backscattered Electron Image
- Image extension element maps record extraordinary detail

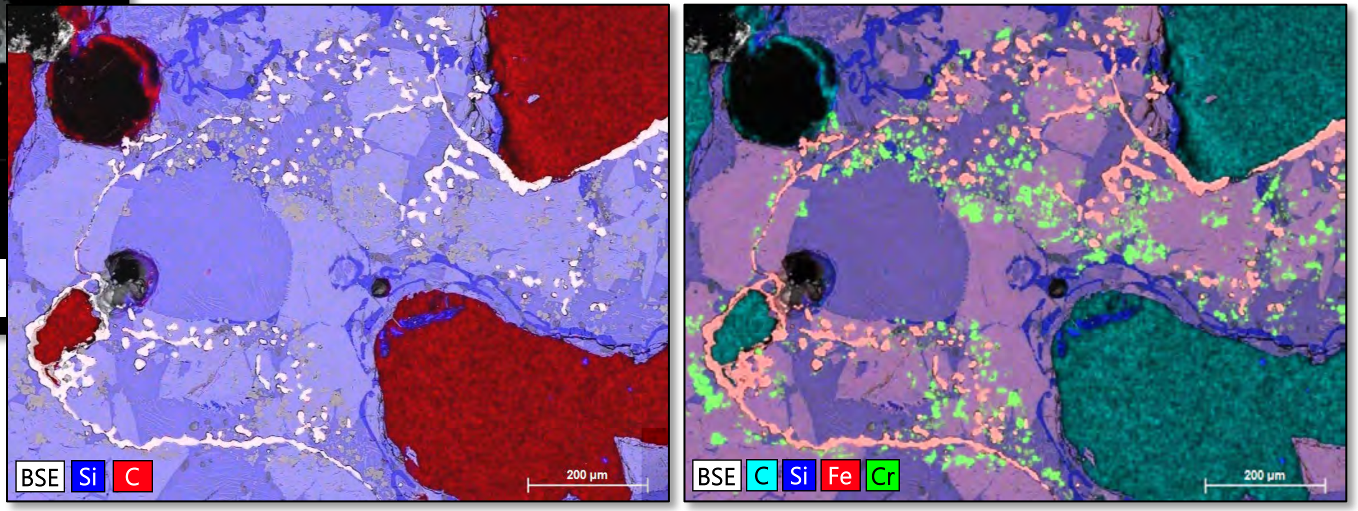
Archaeological ceramics
Experimental iron ore smelting vessel



- Detail on recrystallization processes are revealed in detailed BSE and element maps

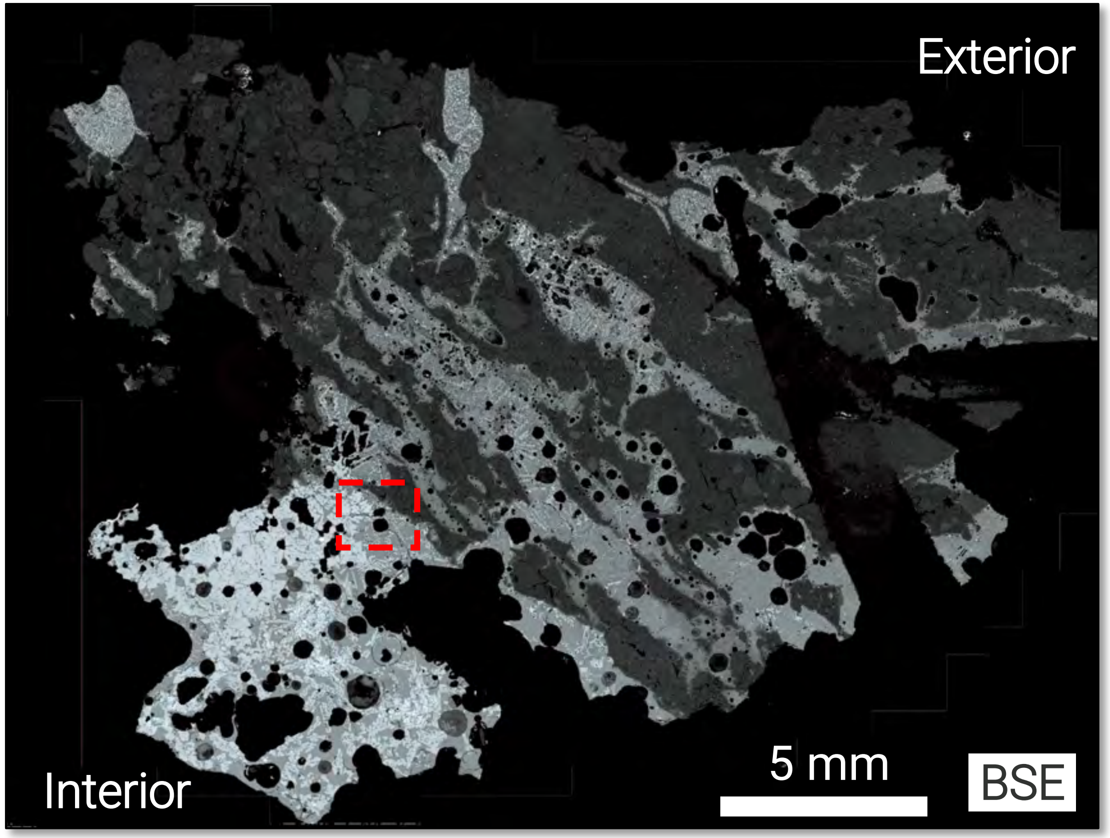
100x mag., 1327 x 968 µm^2 , 1.7 µm pixel size, 64 µs / px, 20 cycles, 10 min meas. time

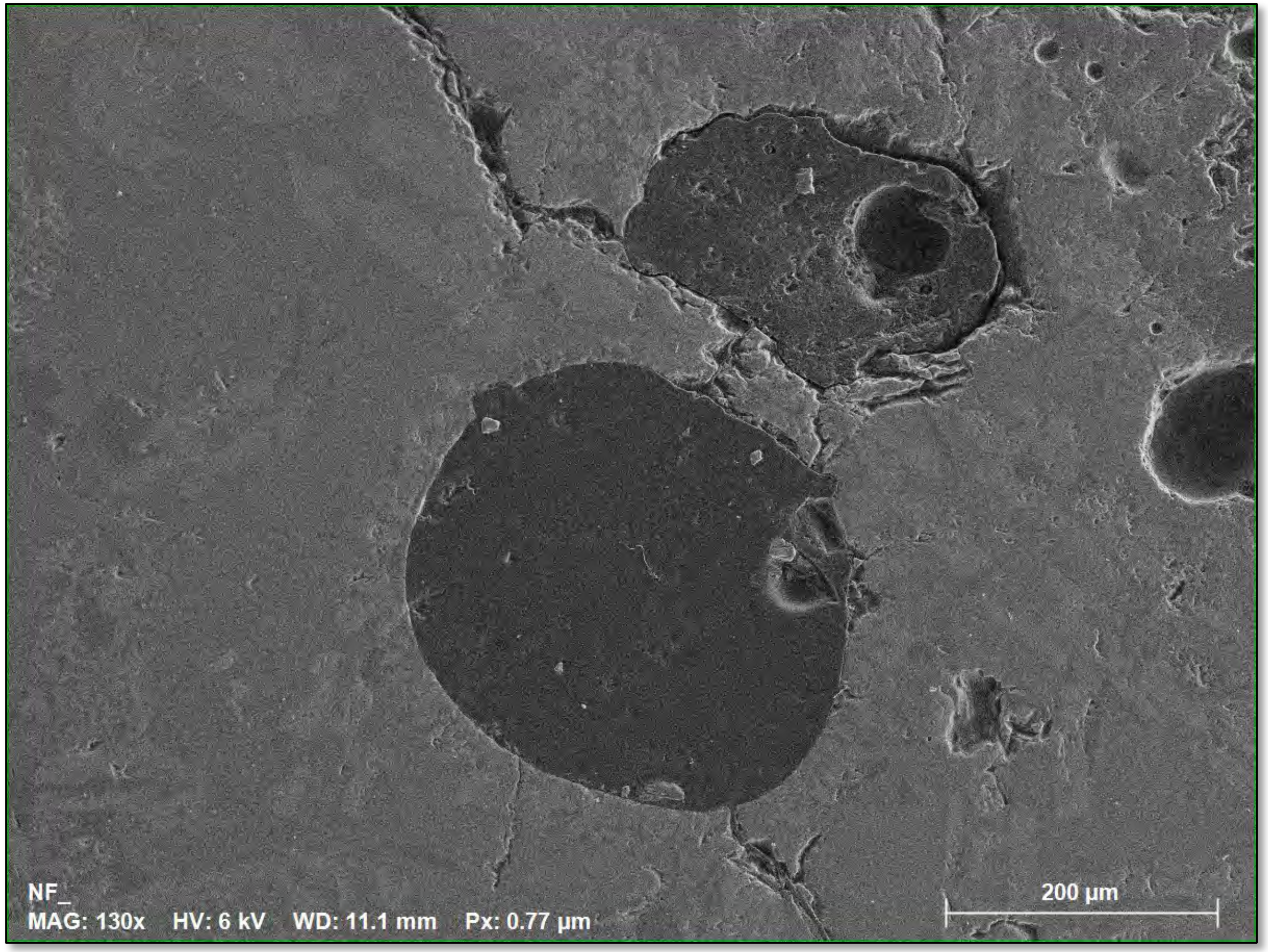




120x mag., 1106 x 806 µm^2 , 1.4 µm pixel size, 64 µs / px, 20 cycles, 10 min meas. time

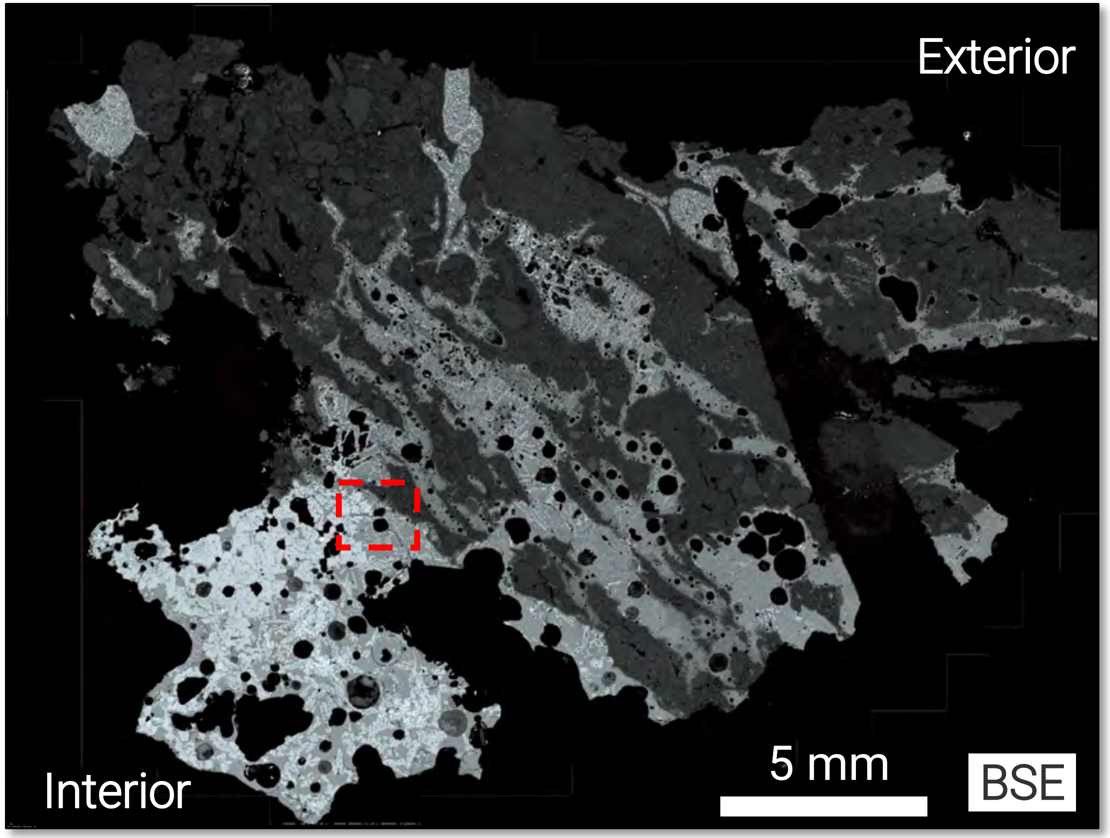
Archaeological ceramics
Experimental iron ore smelting vessel

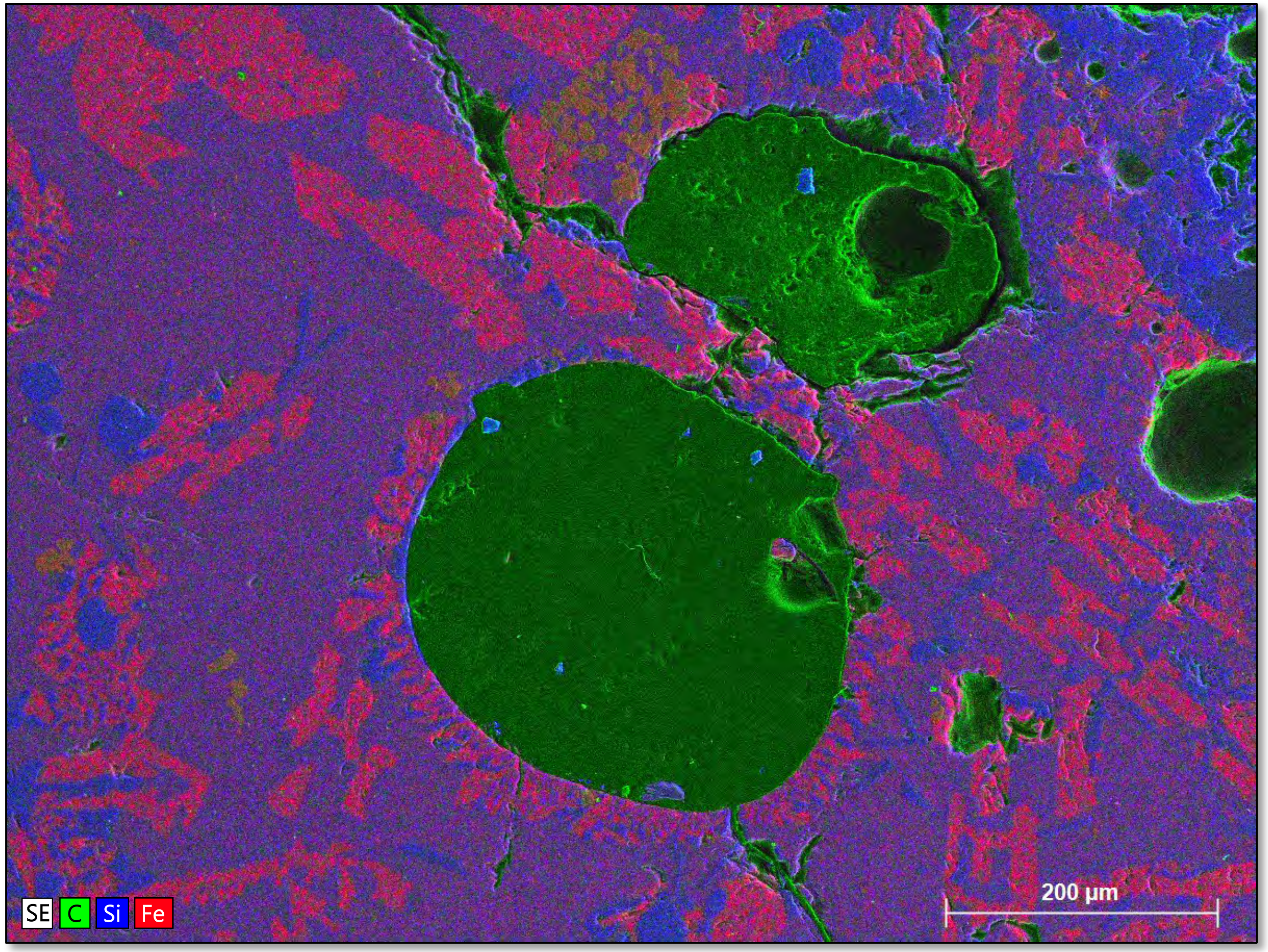




130x mag., 921 x 691 µm^2, 0.77 µm pixel size, 4 µs / px, 148 cycles, 10 min meas. time

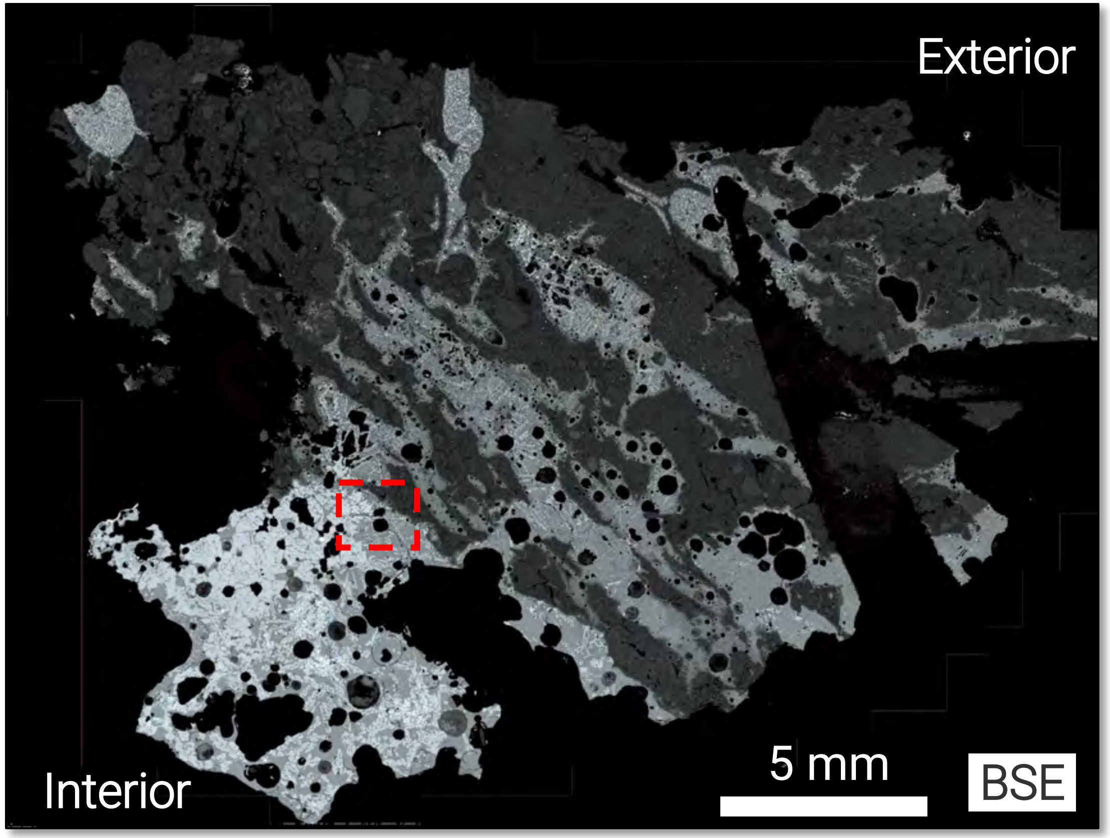
Archaeological ceramics
Experimental iron ore smelting vessel

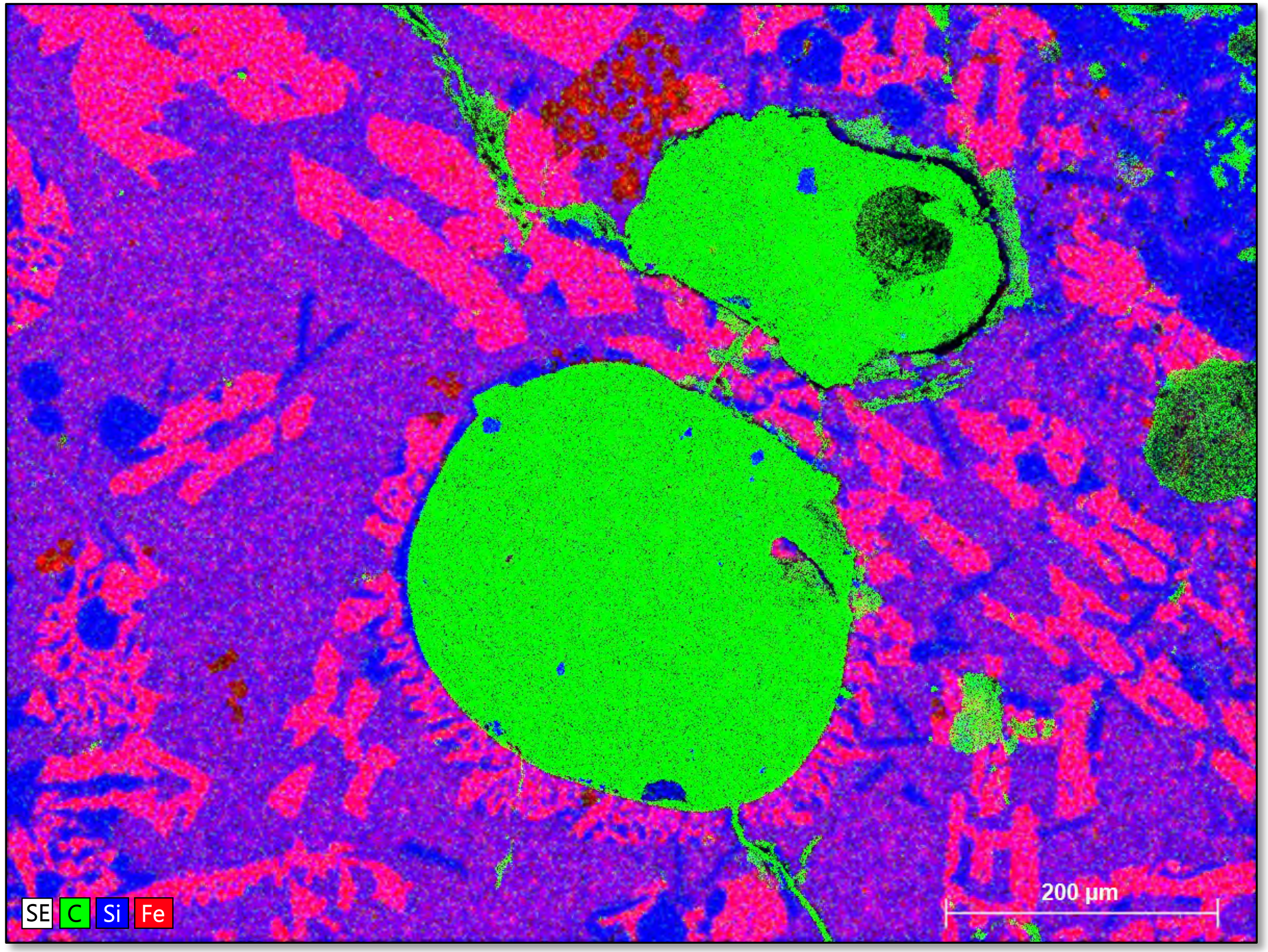




130x mag., 921 x 691 µm^2, 0.77 µm pixel size, 4 µs / px, 148 cycles, 10 min meas. time

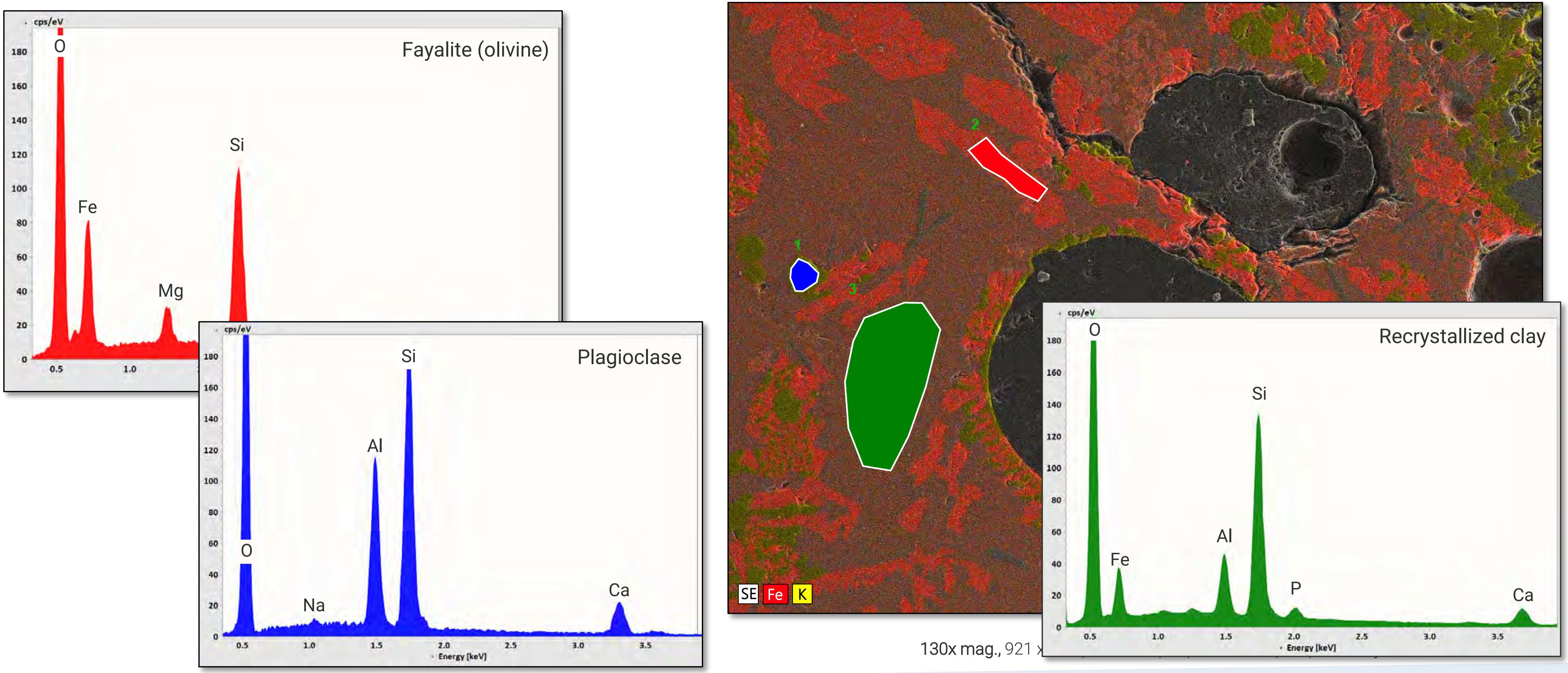
Archaeological ceramics
Experimental iron ore smelting vessel

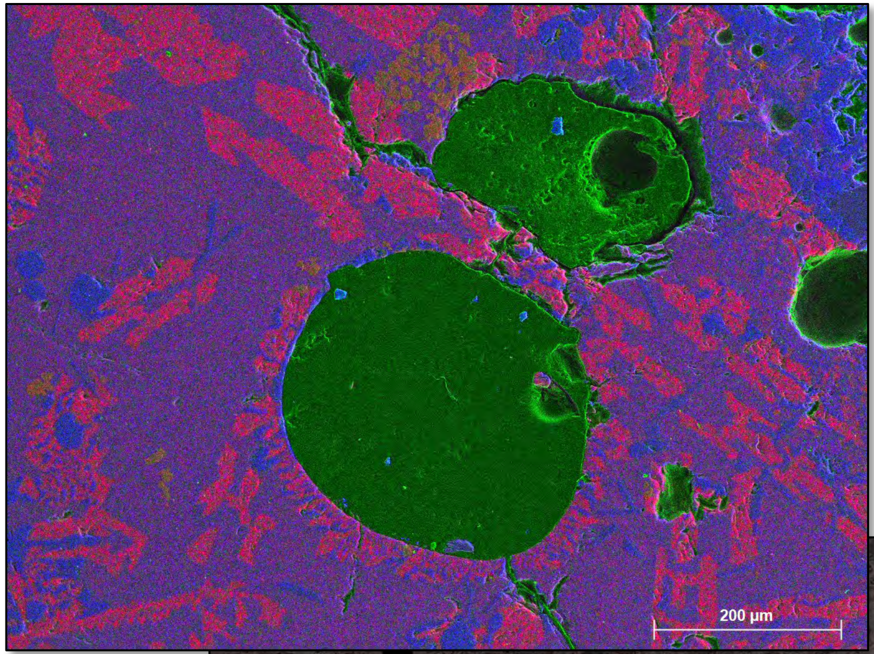


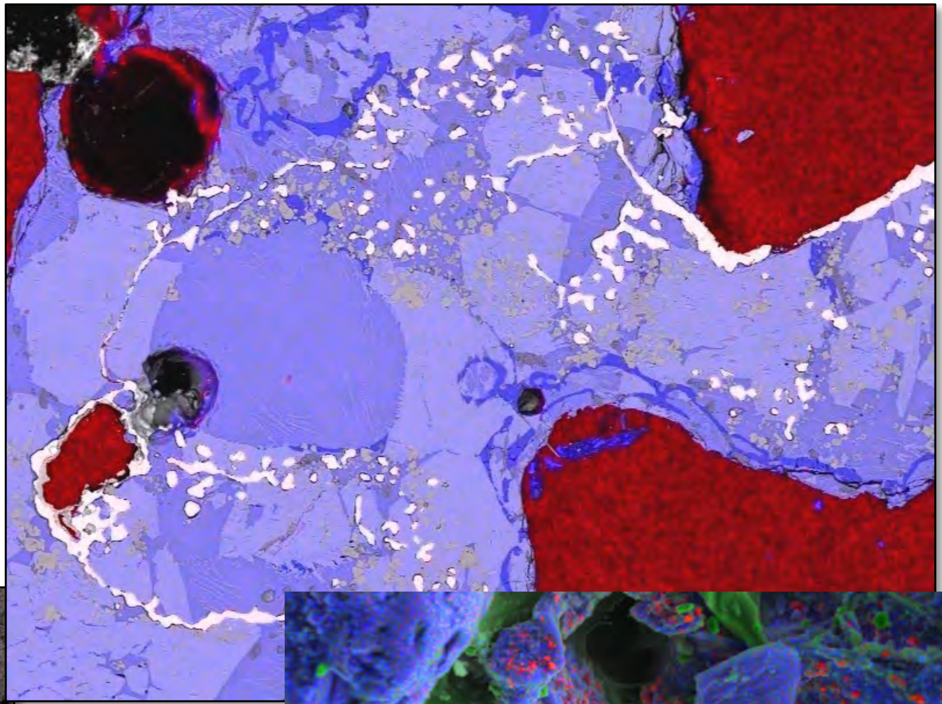


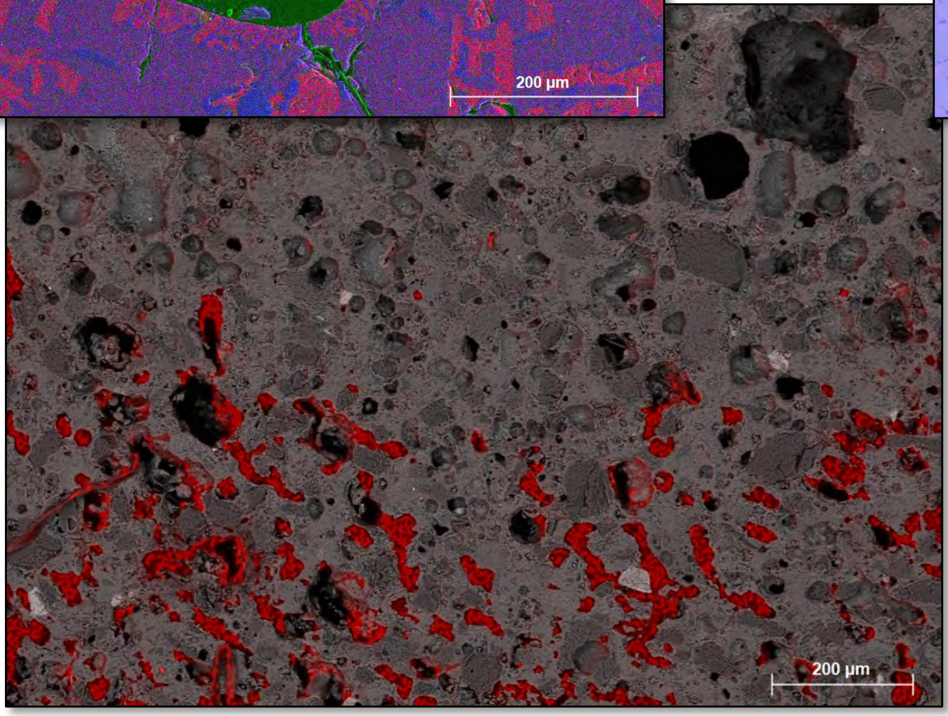
130x mag., 921 x 691 µm^2, 0.77 µm pixel size, 4 µs / px, 148 cycles, 10 min meas. time

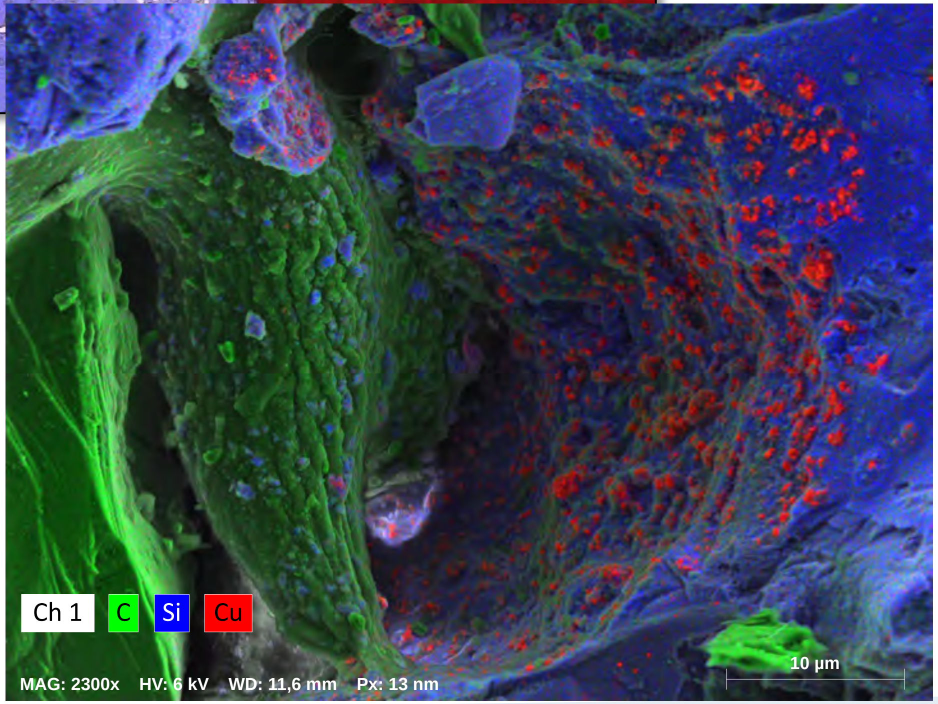
Experimental iron ore smelting vessel




200 µm



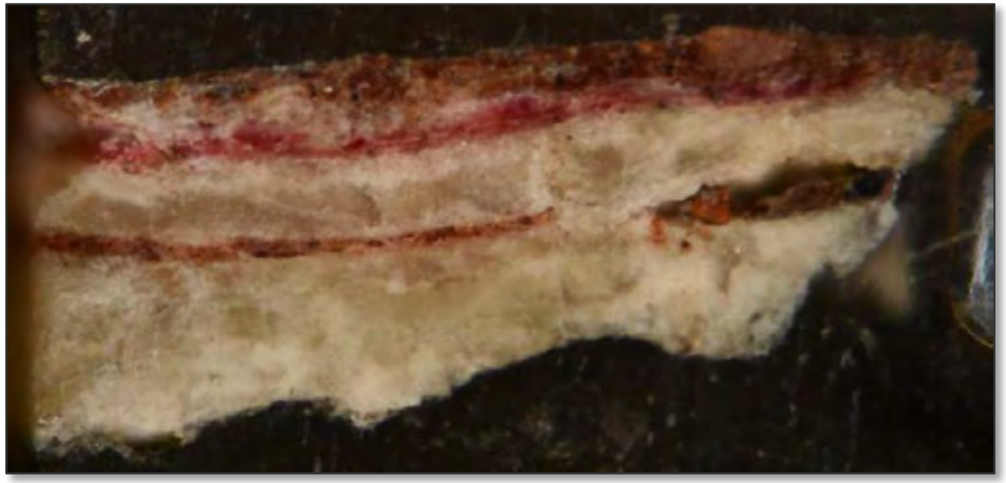

200 µm


Ch 1
C
Si
Cu
10 µm
MAG: 2300x HV: 6 kV WD: 11,6 mm Px: 13 nm

SEM-EDS ANALYSIS IN CULTURAL HERITAGE STUDIES

Example 2: Getting to the detail of pigment components – Da Vinci's *The Last Supper*

Paint cross-section analysis
The Last Supper (Leonardo da Vinci)

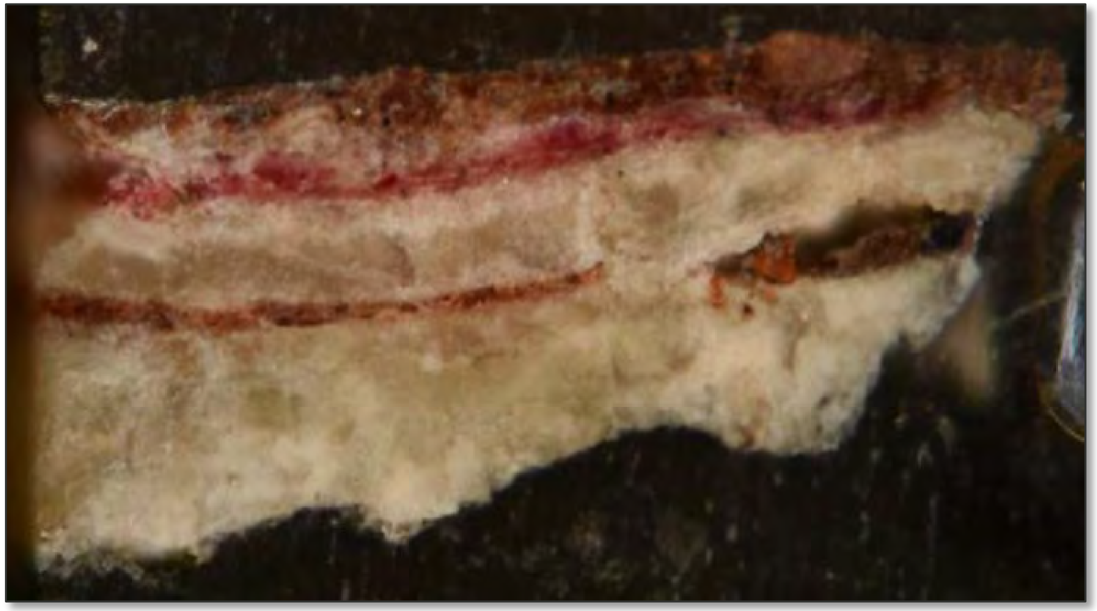


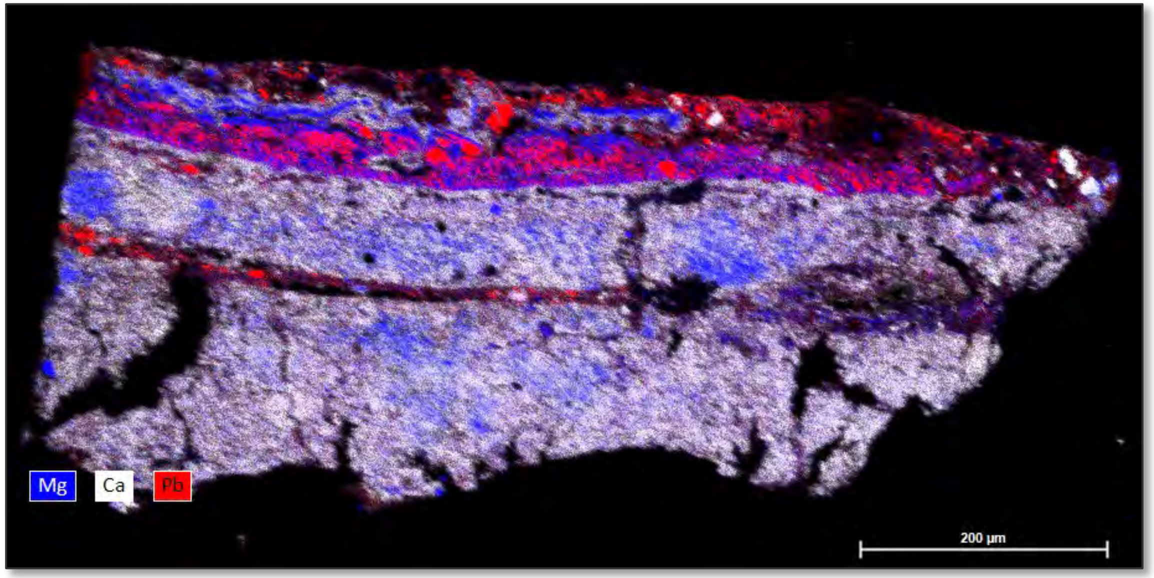
Optical light image of the paint cross-section sample (mounted in epoxy)

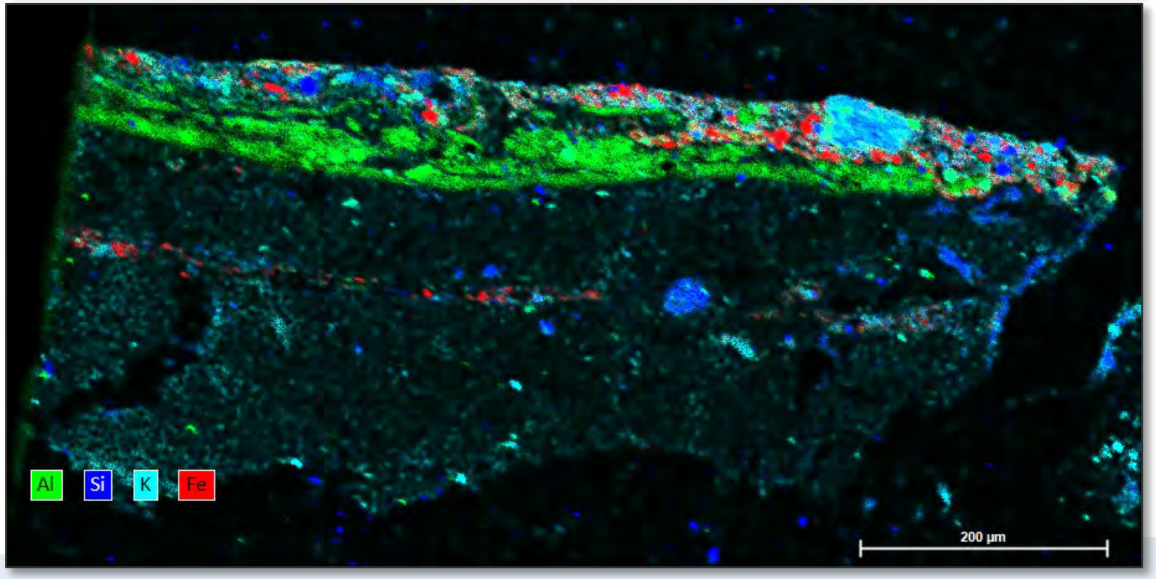
- The wall painting of The Last Supper was executed by Leonardo for the Refectory of Santa Maria delle Grazie in Milan between 1494 and 1498.
- Sample provided courtesy of the ArtIS Laboratory, Politecnico di Milano, through collaboration with Dr. Marta Ghirardello

- SEM – EDS analysis conducted using
  - Field Emission SEM
  - XFlash® FlatQUAD annular detector

Paint cross-section analysis
The Last Supper (Leonardo da Vinci)

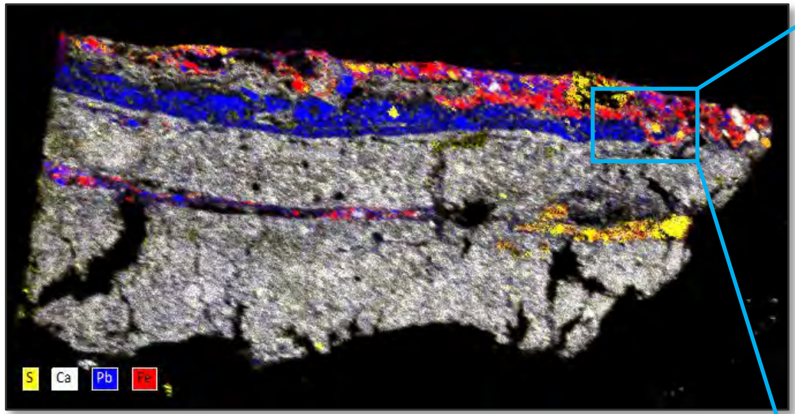


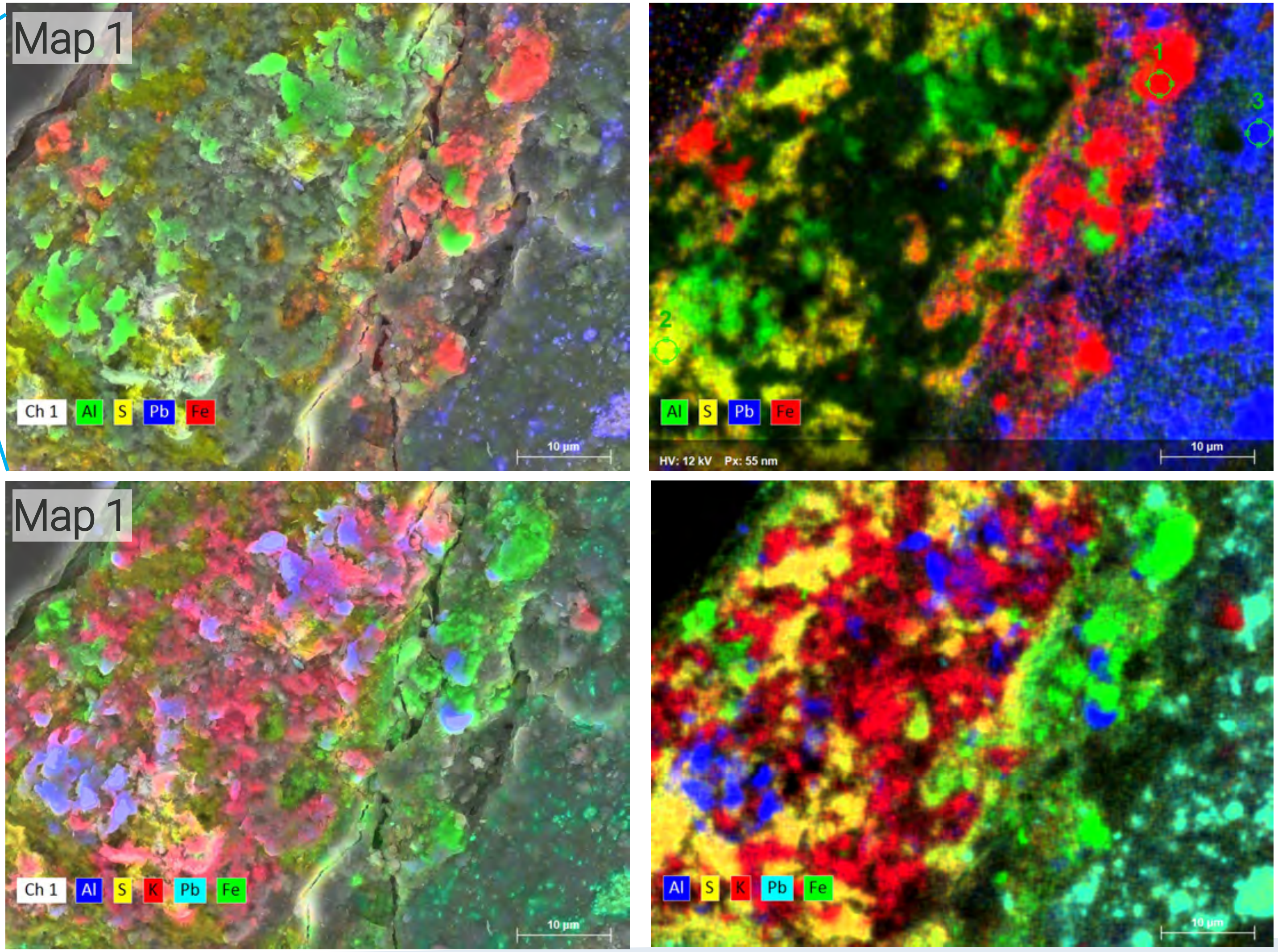




- Preparatory layers of calcite ($CaCO_3$) mixed, Pb-white ($2PbCO_3{\cdot}Pb(OH)_2$), and "Magnesium"
- Interior and exterior red layers: pigment mixtures that include Si, Al, K, Fe.

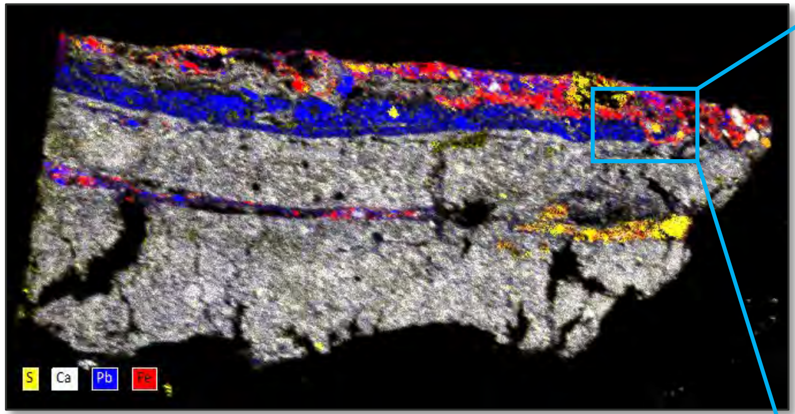
Paint cross-section analysis
The Last Supper (Leonardo da Vinci)



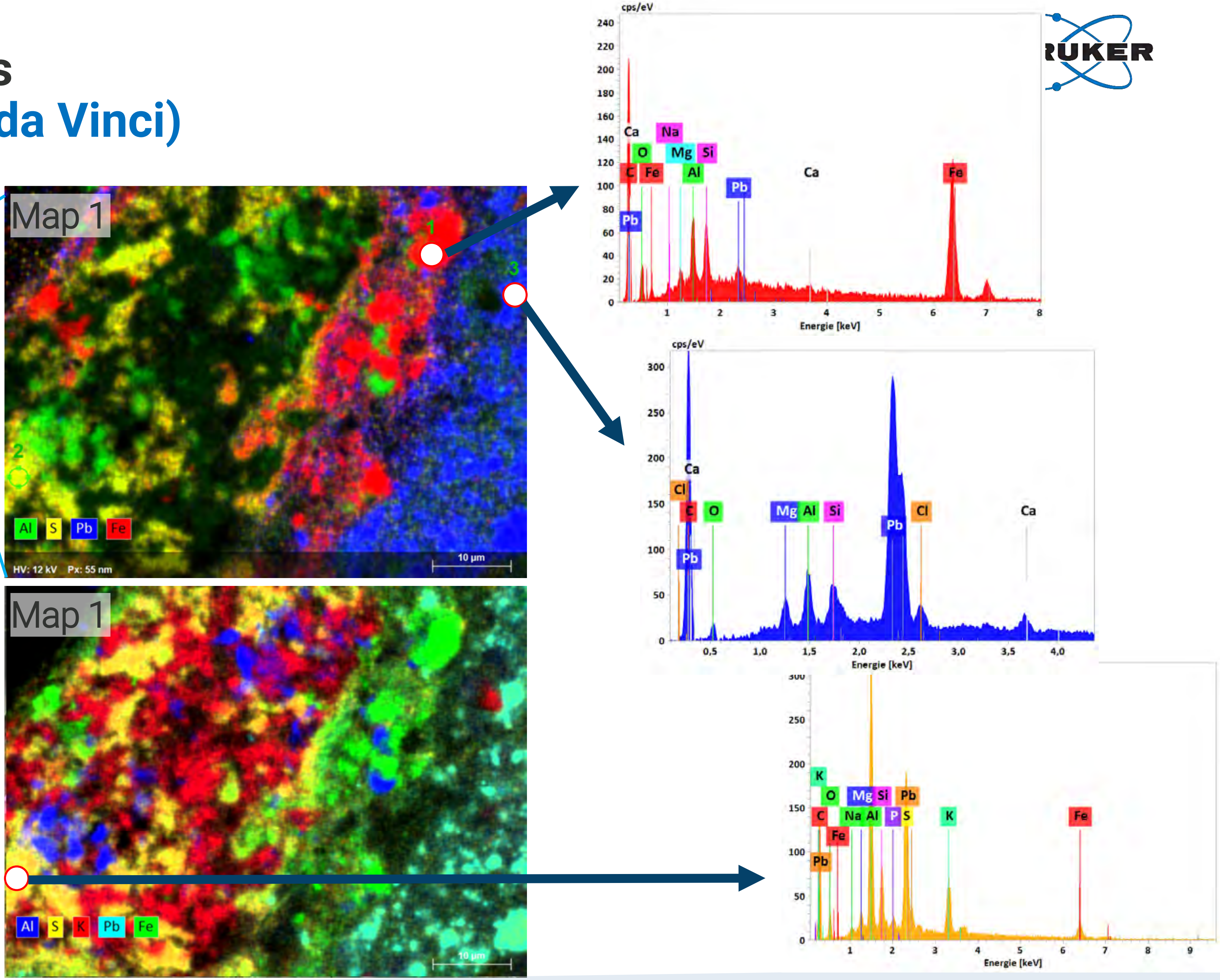


- Mapping at this scale reveals the intricate and complex mixtures

Paint cross-section analysis
The Last Supper (Leonardo da Vinci)

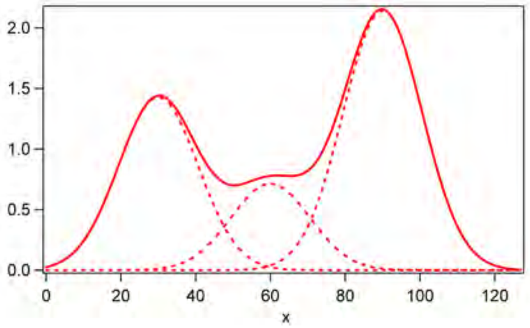


- Mapping at this scale reveals the intricate and complex mixtures
- Spectra can be extracted from each pixel in the map for element identification and quantification

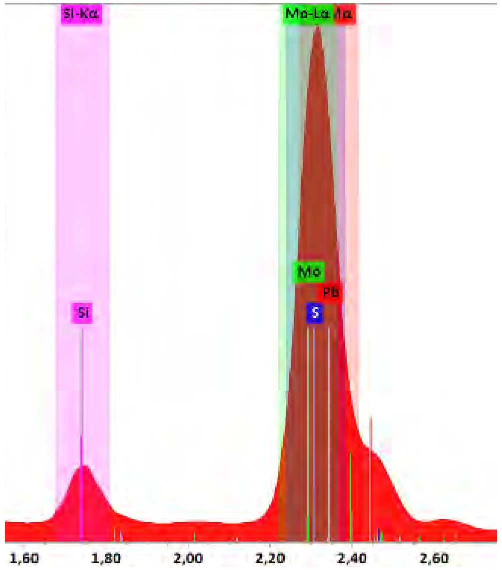


Resolving peak overlaps in spectra and maps
Deconvolution

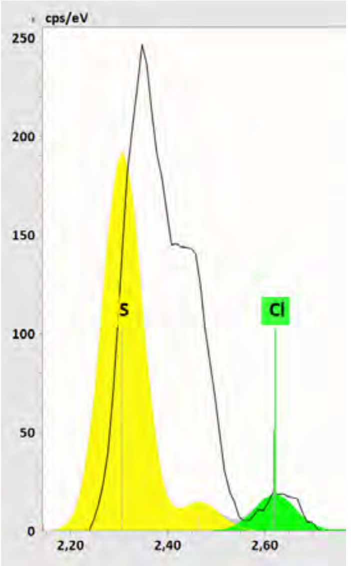
- ***What is deconvolution?***
  - Treat a spectrum as a mathematical function *(f)* which is the sum of n individual spectra, where n=number of elements present in the spectrum
  - Calculate the individual functions by minimizing the difference between the original function and the sum of individual functions



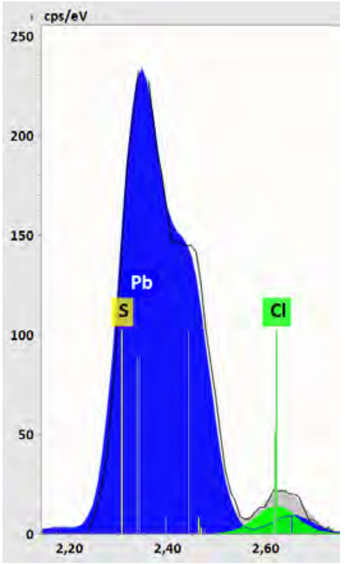
$$f = f_1 + f_2 + f_3 + \cdots$$



Measured spectrum
Which element(s)?

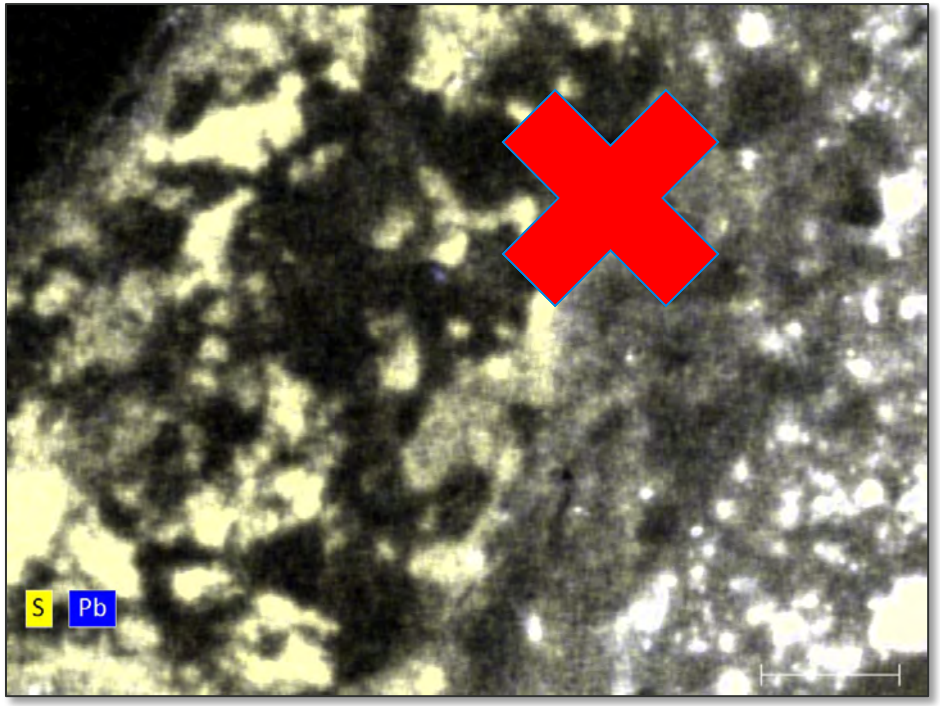


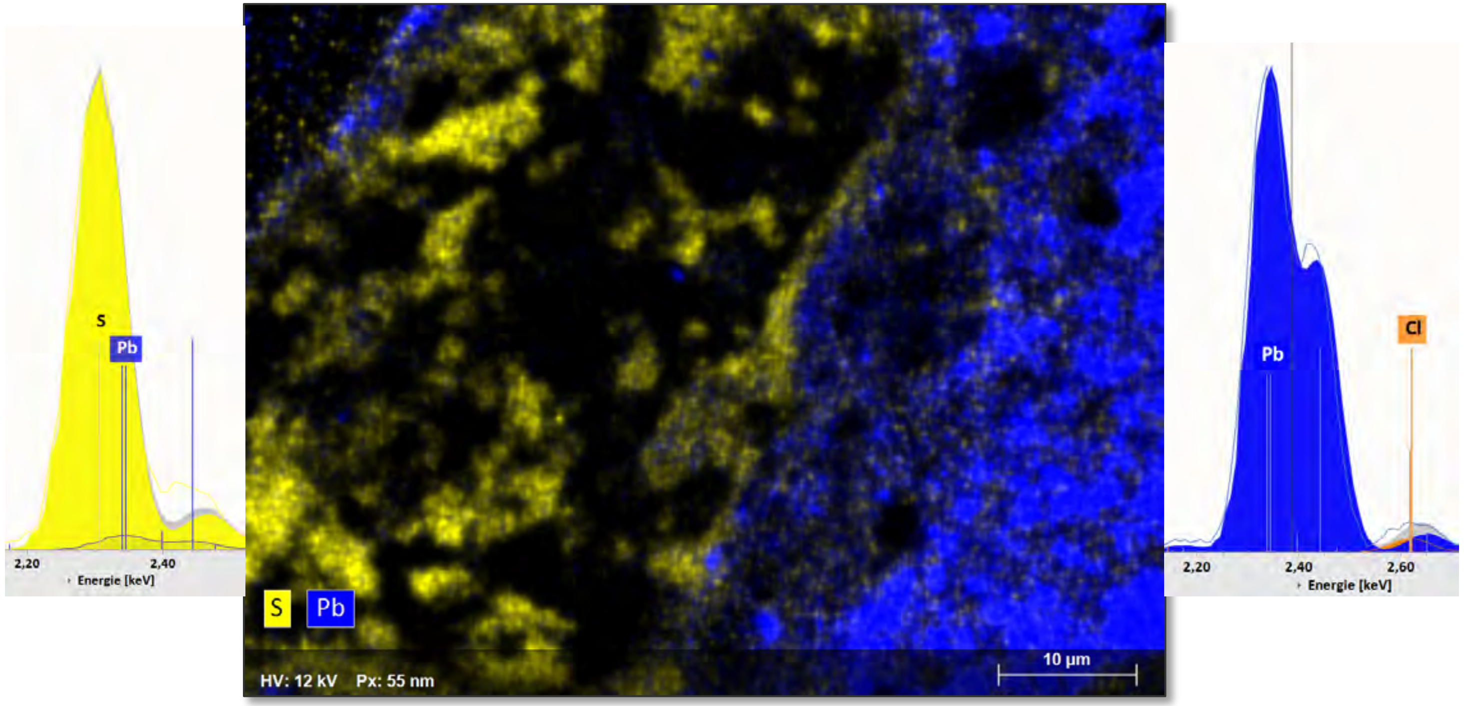
"Best fit"
incorrect element



"Best fit"
correct element

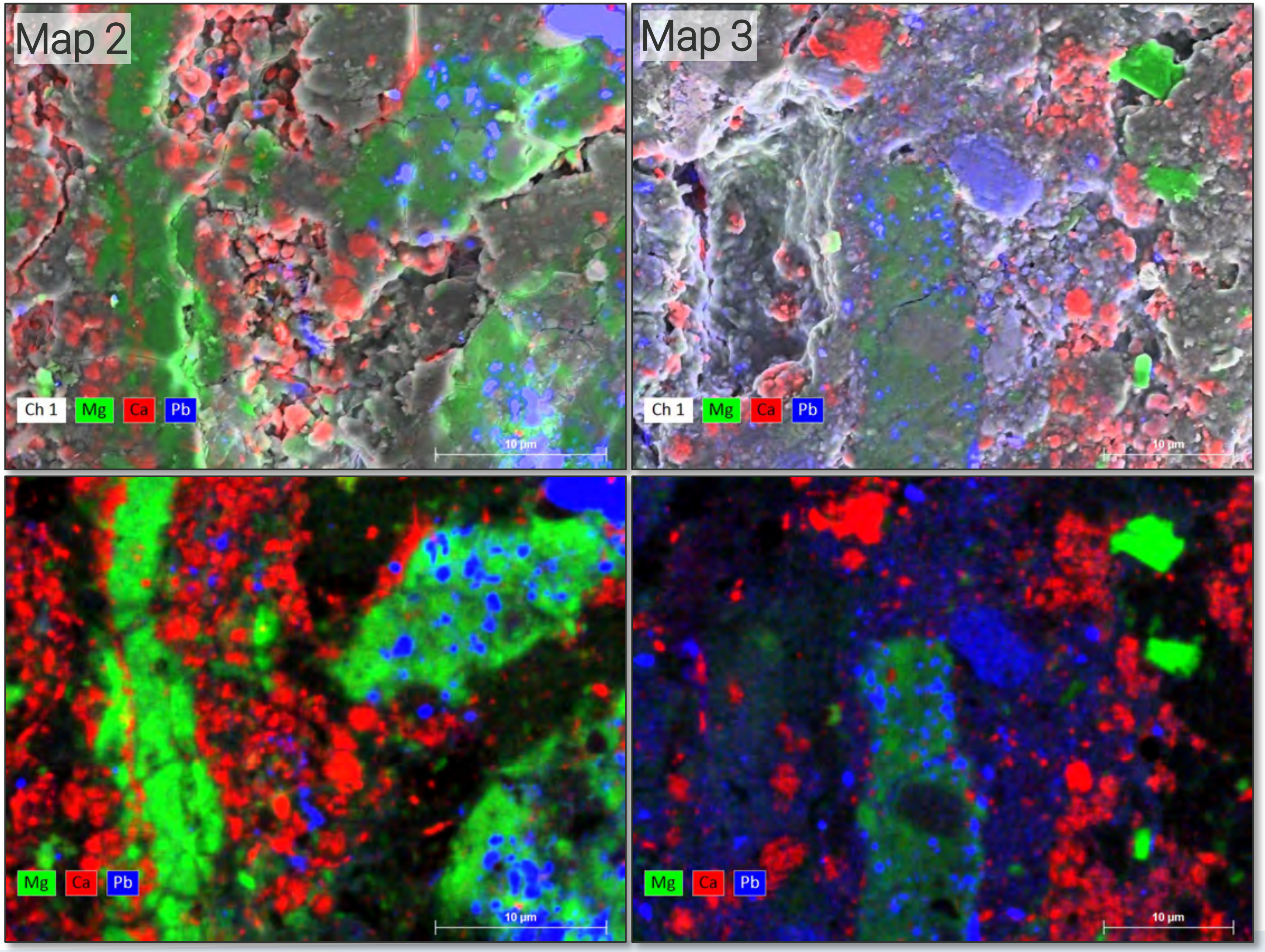
Resolving peak overlaps in spectra and maps
Deconvolution





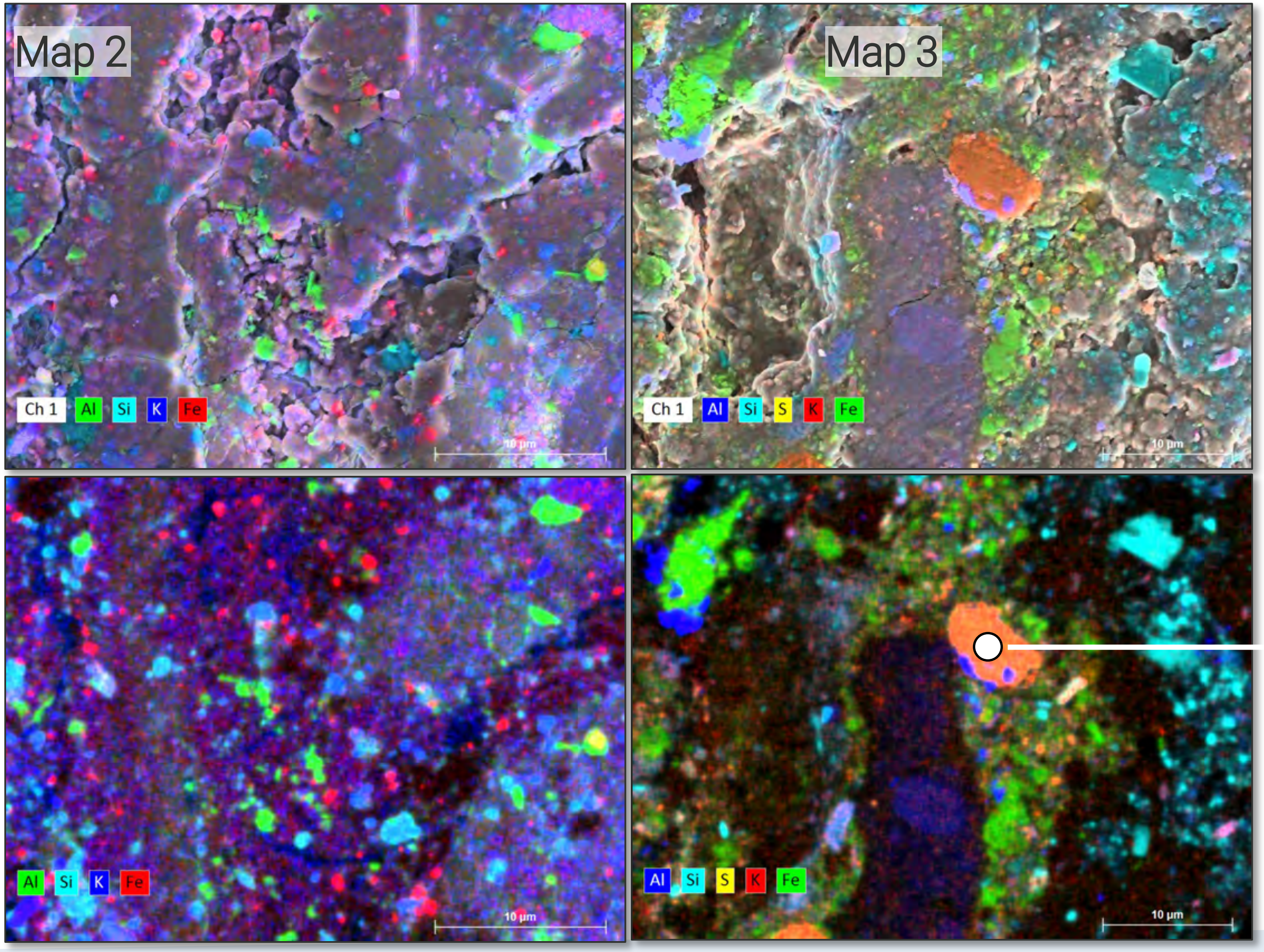
- Overlapping elements like Pb/S/Mo can be separated during map acquisition and in the spectrum
- Reveals true element distribution and correct identification of pigment components

Paint cross-section analysis
The Last Supper (Leonardo da Vinci)

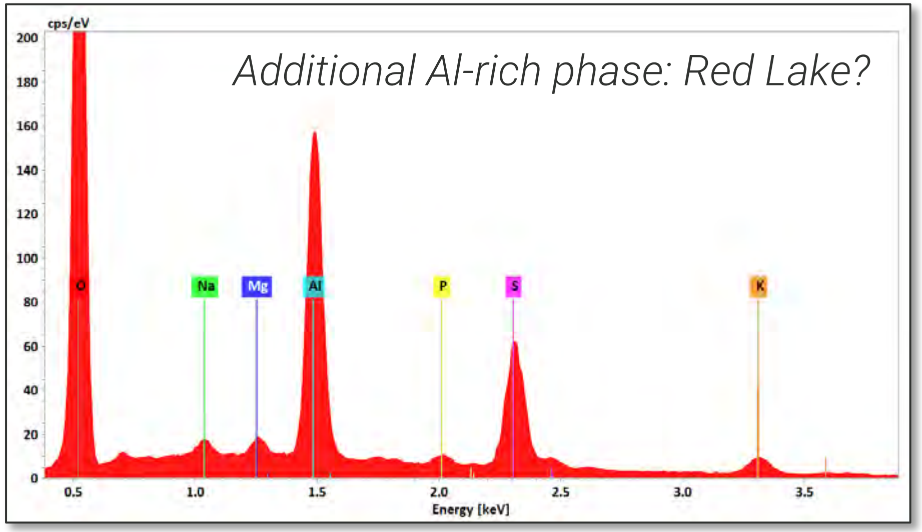


- Detailed view of the preparation and base layers
  - Ca: limestone (calcite)
  - Mg: Nesquehonite ($MgCO_3.3H_2O$)
  - Pb: some distributed particles of Pb-white ($2PbCO_3{\cdot}Pb(OH)_2$)

Paint cross-section analysis
The Last Supper (Leonardo da Vinci)

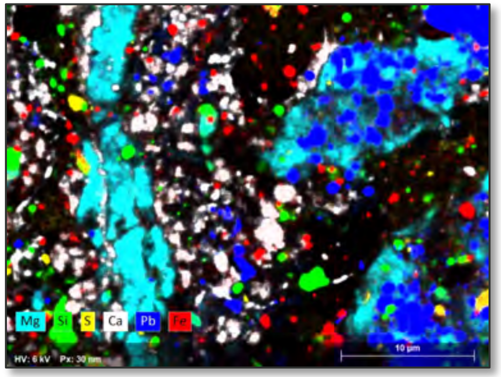


- Mixed components – red ochre with sand?
  - Si: quartz
  - Si + K + Al: feldspar
  - Fe: red ochre



Paint cross-section analysis
The Last Supper (Leonardo da Vinci)

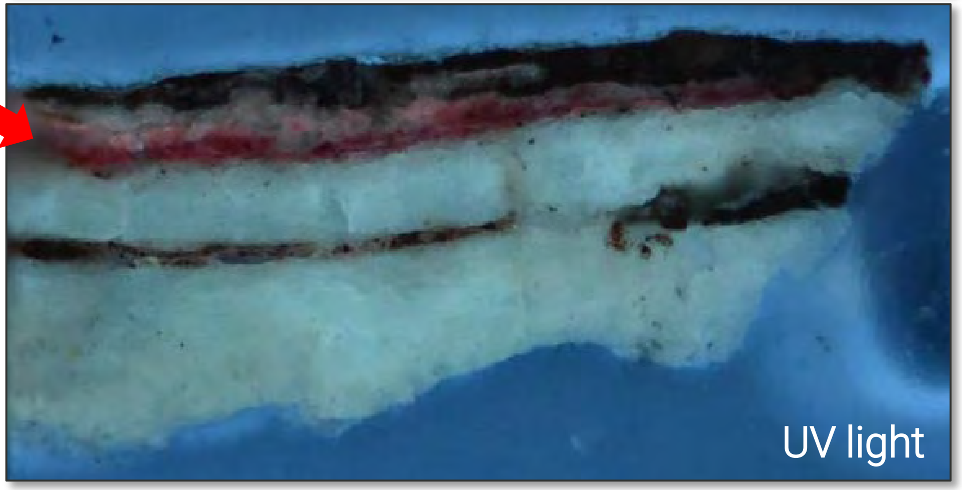
- Readily identified the main components of the cross section, even at "low" magnification
  - Calcite, magnesium, Pb-white preparation layers
- Composition of the bright red layer close to the top of the section aligns with Red Lake pigment compositions
  - Correlates with UV images (see right)
- Additional element maps demonstrate the complexity of mixtures used in additional red-brown pigment layers



Complex pigment mixtures

$CaCO_3$ + $MgCO_3$ base prep

Red lake pigment



CULTURAL HERITAGE UNDER THE MICROSCOPE

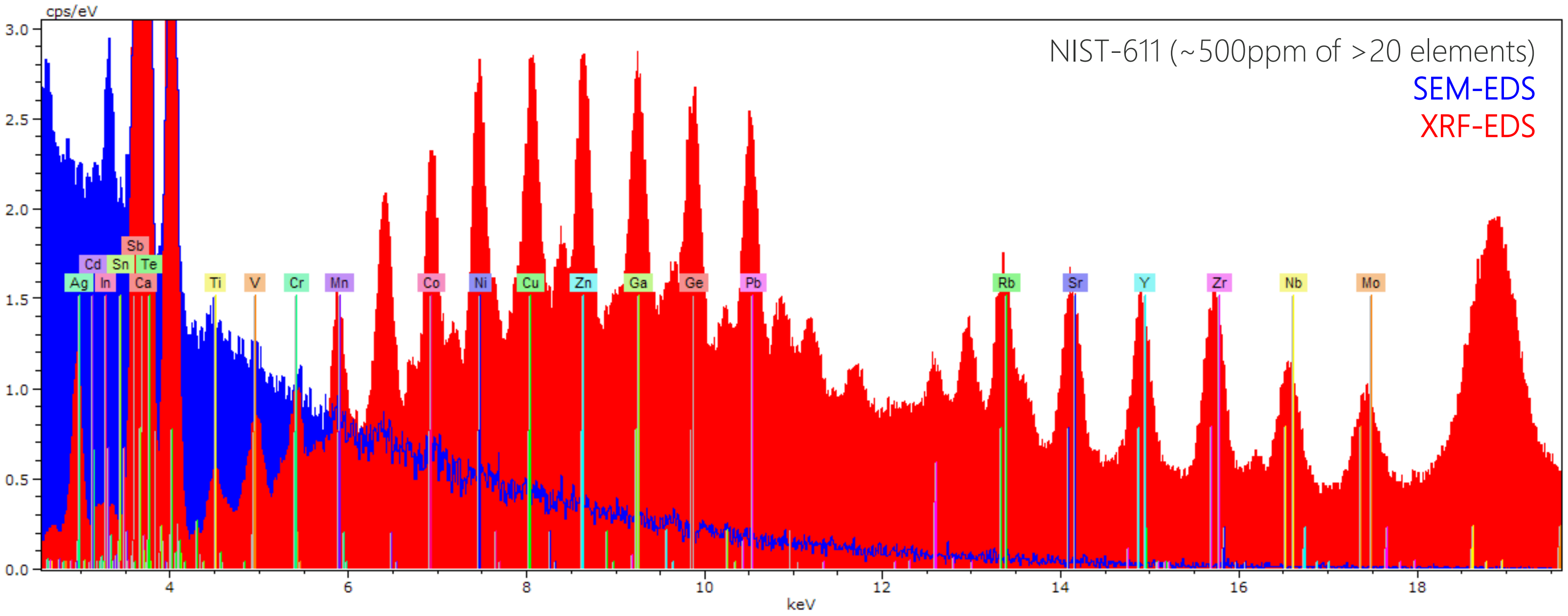
Example 3: Integrating SEM-based µXRF with electron-beam EDS analysis: A study of large-scale Mesoamerican obsidian tablets

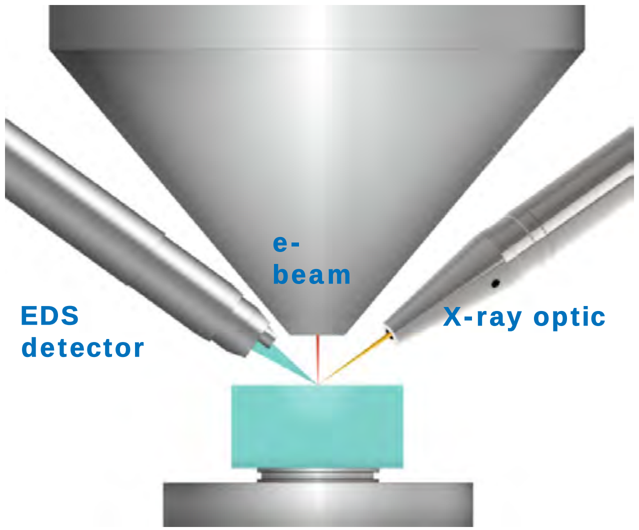
Application study by Meredith Sharps[1], Marian Martinez[2], Michael Brandl[3], Thomas Lam[1], Edward Vicenzi[1]
[1]Smithsonian Institution, Museum Conservation Institute; [2]National Museum of the American Indian, Cultural Resources Center; [3]Institute for Oriental and European Archaeology, Austrian Academy of Sciences
For more information: *Sharps et al. (2021). Journal of Archaeological Science: Reports, 35, 102781*

µXRF in the SEM
Expanding elemental capabilities

- Limitation of electron source in elemental analysis
  - Best excitation at lower energies
  - Limited ability to excite higher energies characteristic of key trace elements

- X-ray source unlocks access higher energy X-ray lines, and when combined with EDS using an electron source gives the best of both worlds





µXRF in the SEM
Expanding elemental capabilities

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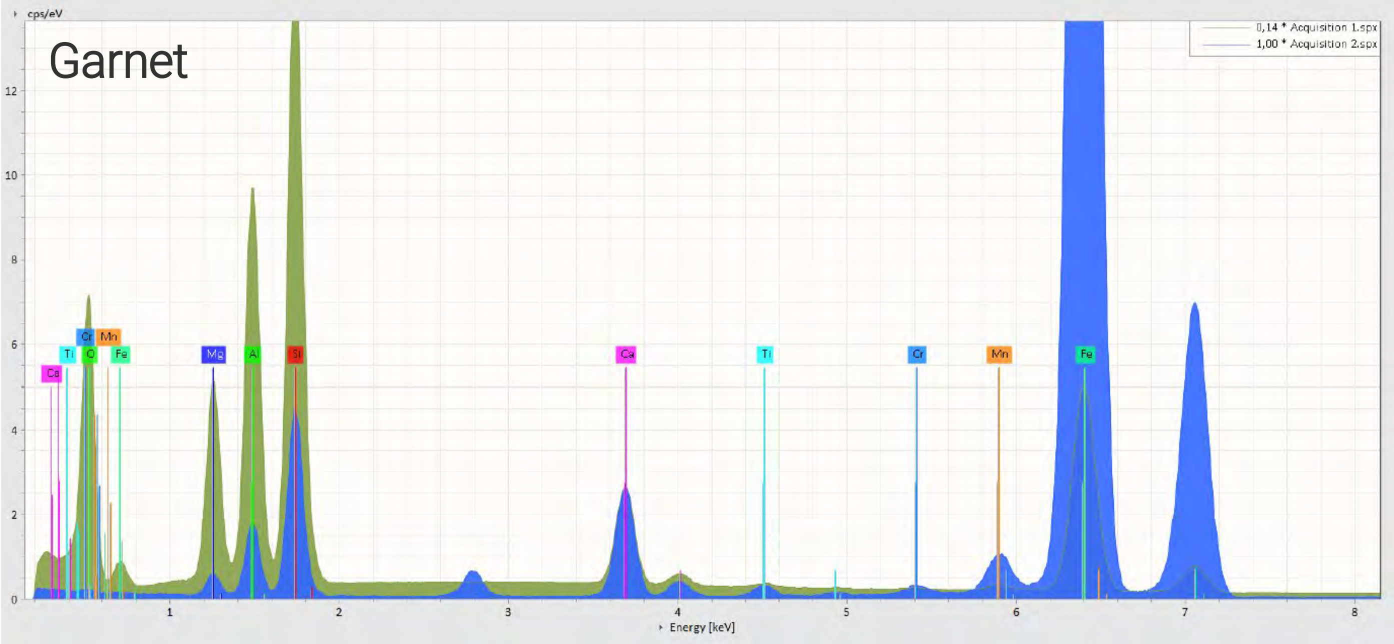
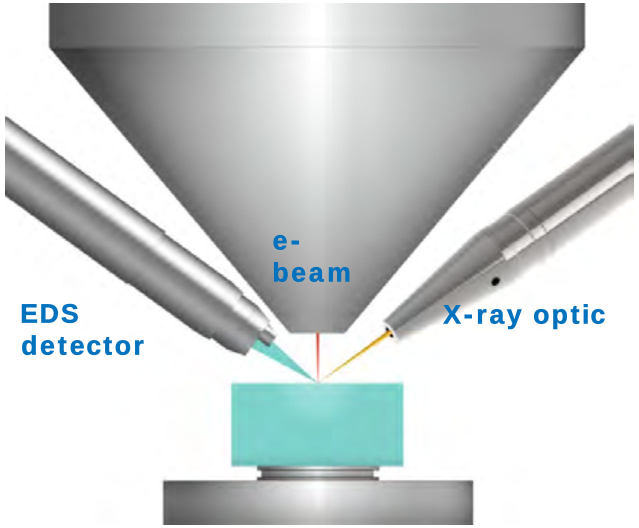
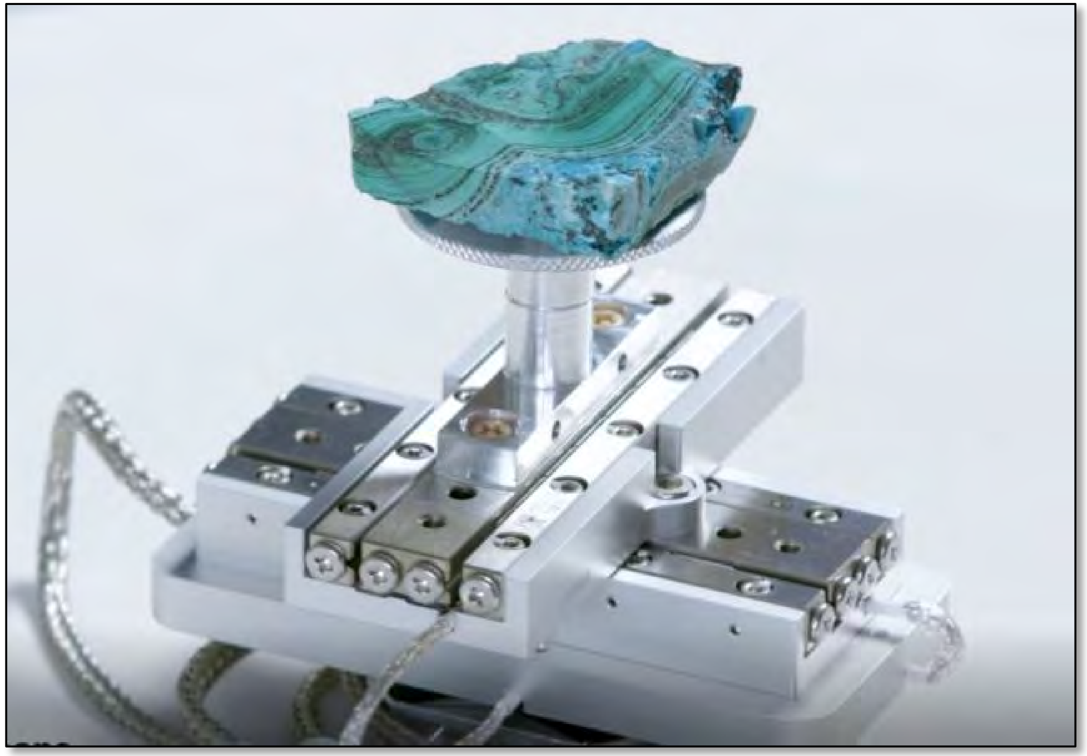
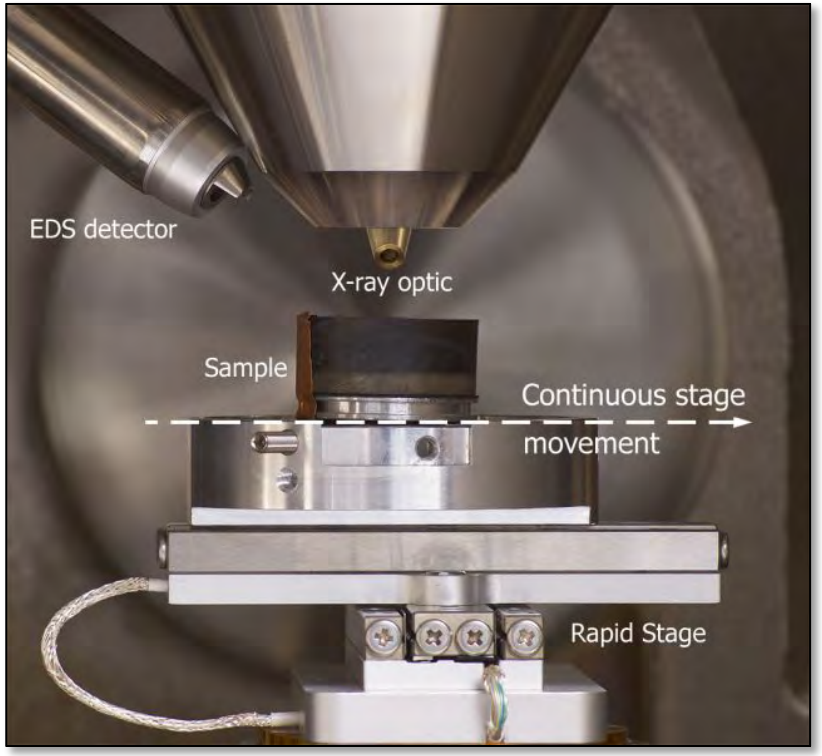




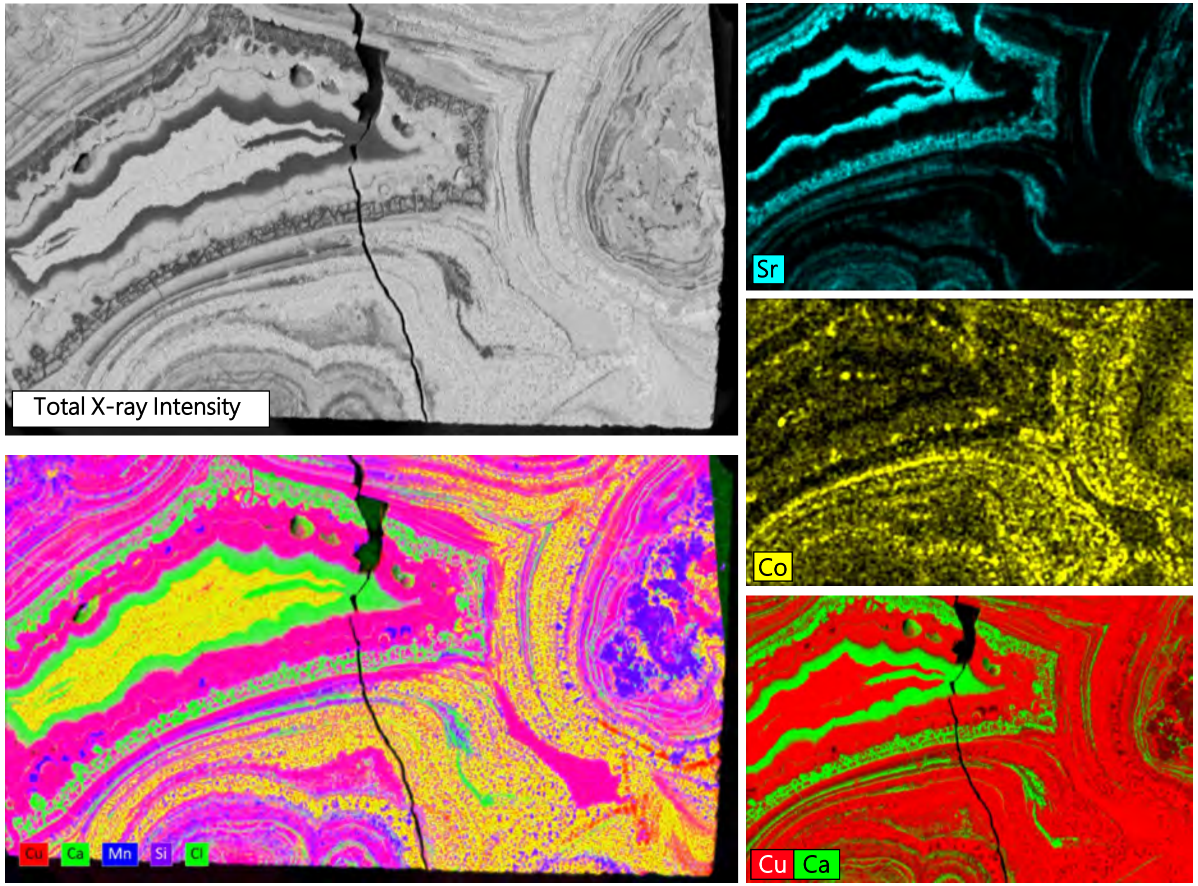
µXRF in the SEM
Rapid mapping using the sub-stage



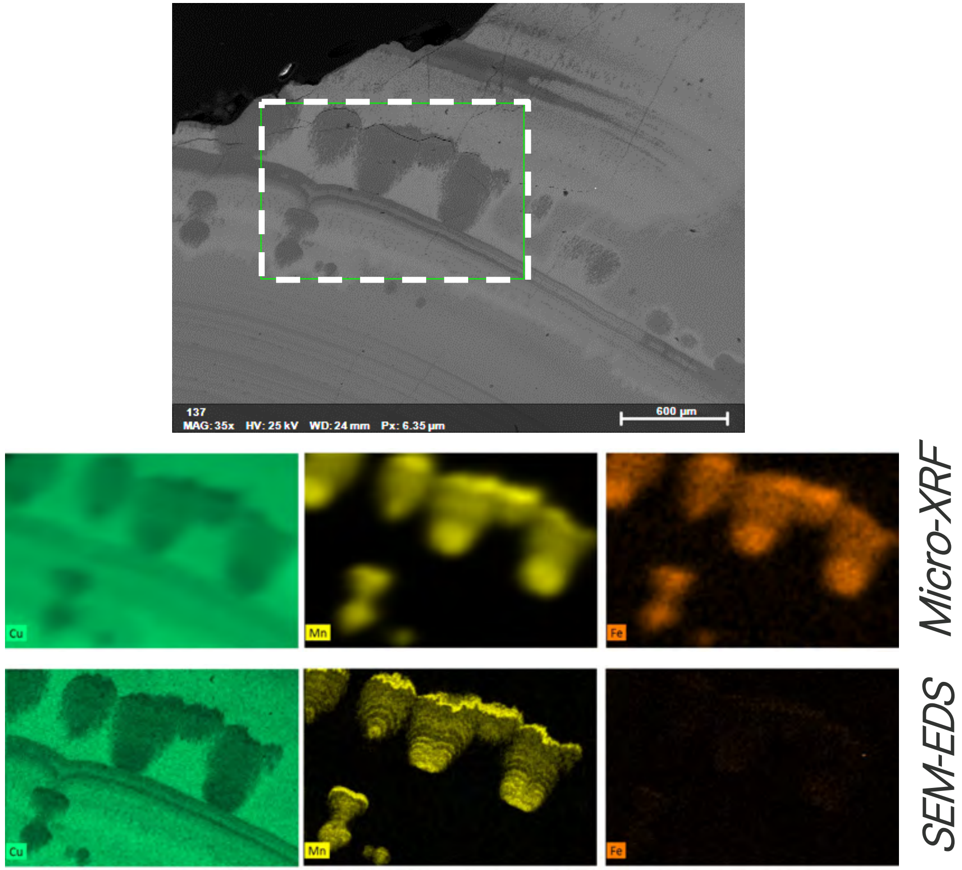


For more information, look for our webinars on the XTrace and rapid mapping stage on demand at www.bruker.com/webinars

µXRF in the SEM
Rapid mapping using the sub-stage



Polished Section: 45 x 30 mm



Tube Voltage: Rh at 50 kV
Anode Current: 600 µA
Pixel Spacing: 25 µm
Analytical Time: 101 mins

For more information, look for our webinars on the XTrace and rapid mapping stage on demand at www.bruker.com/webinars

Example: Tandem analysis of large, Mesoamerican obsidian mirrors by SEM-based EDS and micro-XRF

- Obsidian is volcanic glass formed due to rapid eruption and crystallization of lava
- Homogeneous within a flow, but preserve compositions that are distinctive between locations, which allows artefacts to be matched to probable raw source material locations

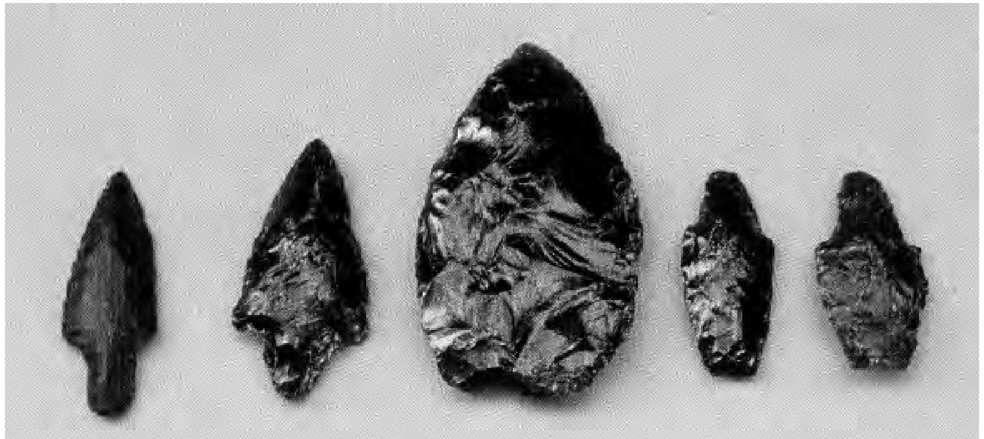


Photo credits: R. Tykot

Sharps et al. (2021). Journal of Archaeological Science: Reports, 35, 102781

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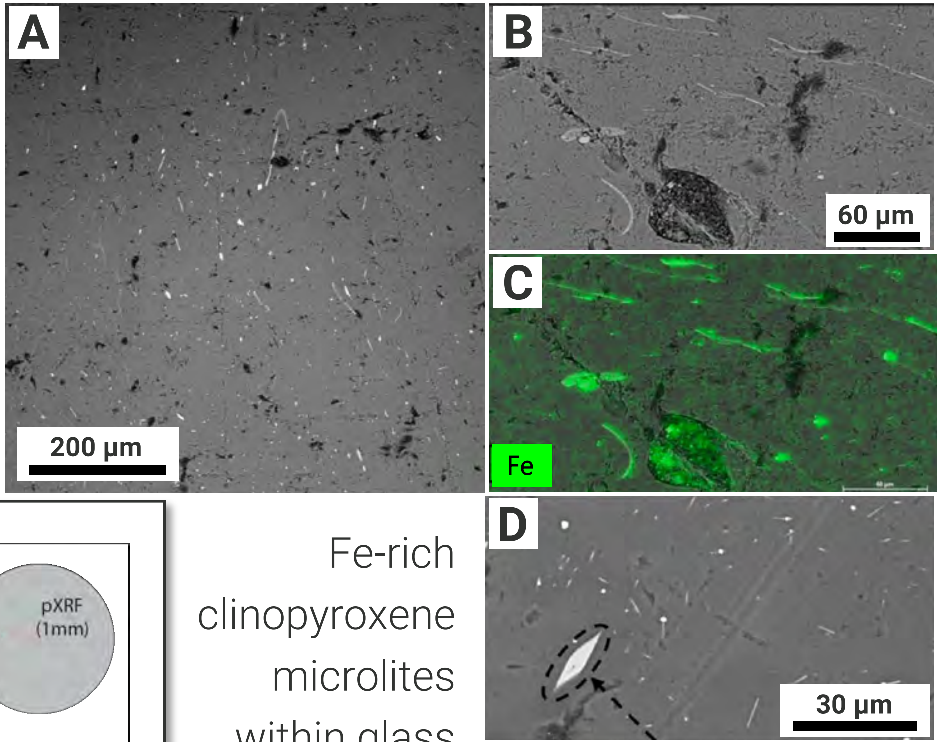
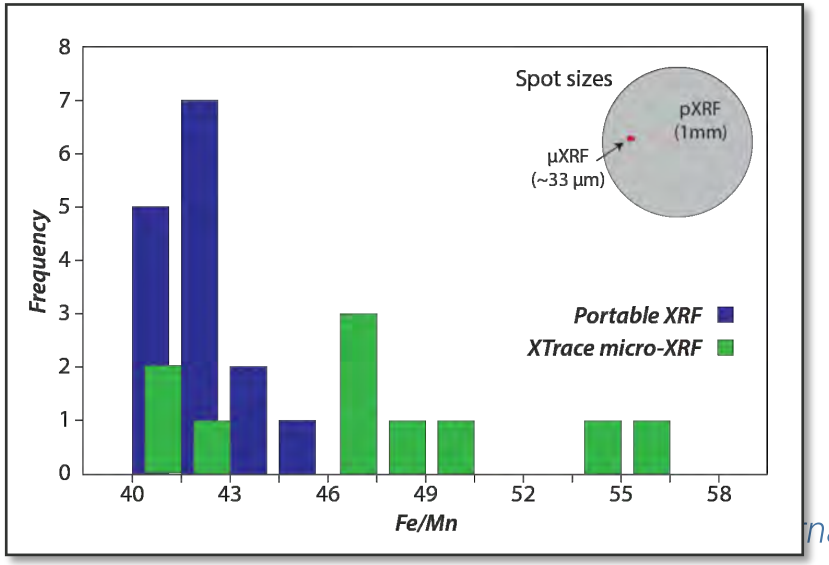


Fe-rich clinopyroxene microlites within glass (obsidian)

- The assumption of homogeneity is not always founded, so more detailed observations may be required
  - SEM imaging
  - Micro-XRF compositional analysis



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Example: Tandem analysis of large, Mesoamerican obsidian mirrors by SEM-based EDS and micro-XRF

1. Homog., black
2. Black, with gray flow banding
3. Brecciated mahogany tablet

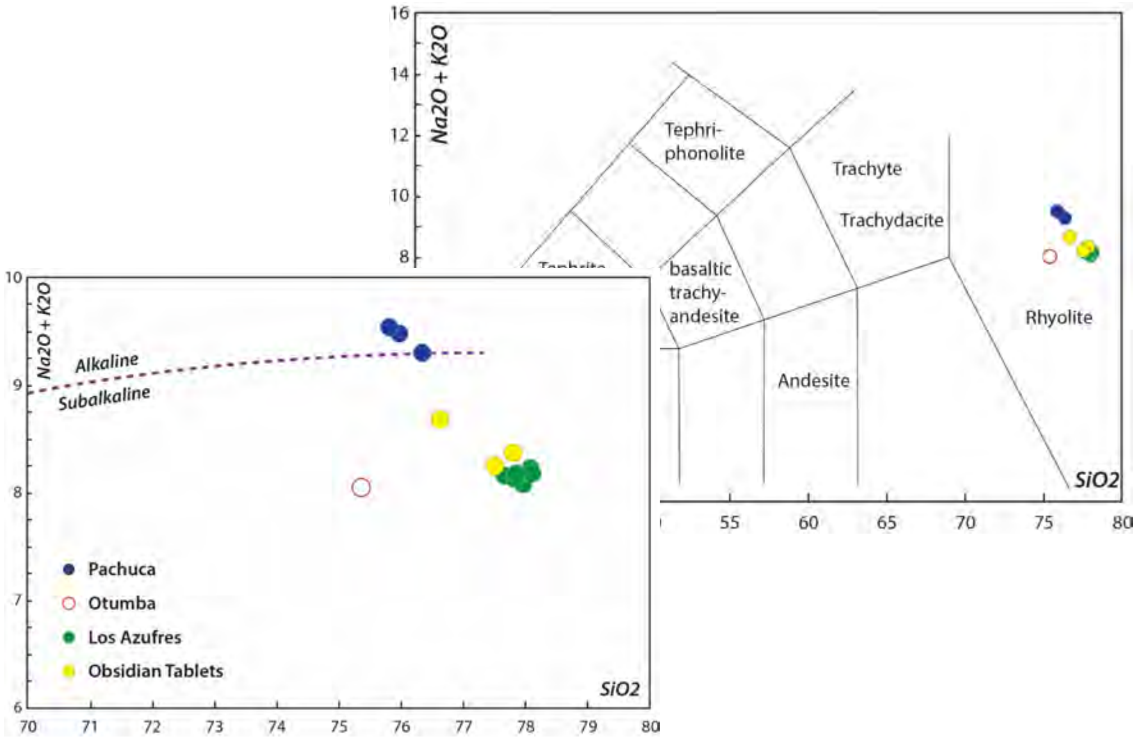
- Polished obsidian "mirrors" likely sourced from the Trans-Mexican Volcanic Belt
  - Such artefacts were produced from pre-Columbian through to colonial times
  - Previously analyzed by pXRF

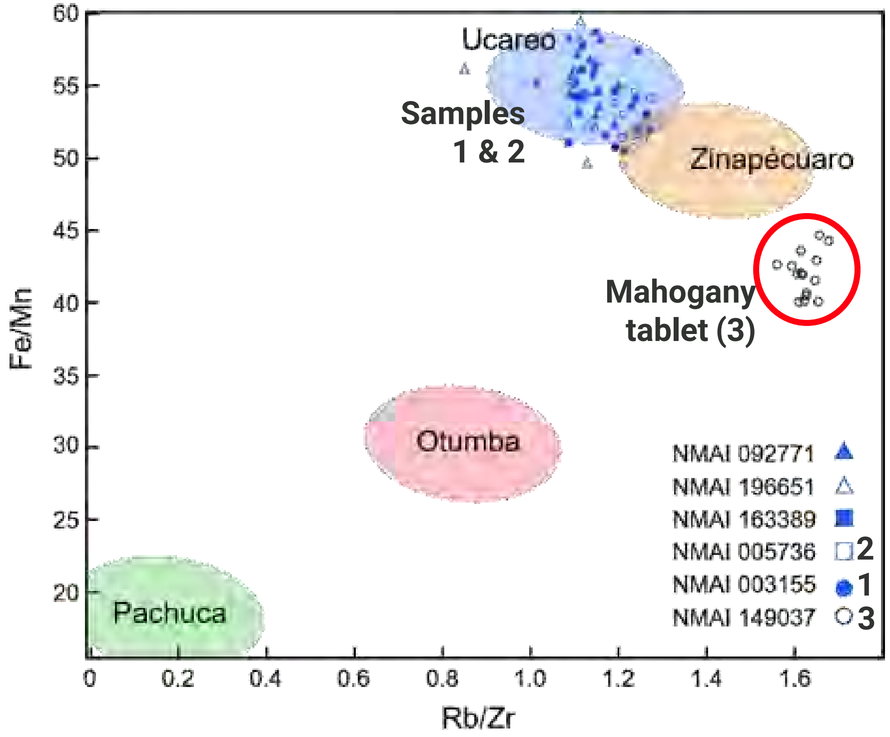
- "Tandem beam" SEM
  - Electron-beam source
  - XTrace µXRF source
    - Characteristic X-rays from both sources measured with Bruker XFlash® 6|60 SDD detector
  - Ran under variable pressure conditions

Sharps et al. (2021). Journal of Archaeological Science: Reports, 35, 102781

Images courtesy of Michael Brandl, modified from Martinez et al., 2021, Sharps et al., 2021)

Example: Tandem analysis of large, Mesoamerican obsidian mirrors by SEM-based EDS and micro-XRF

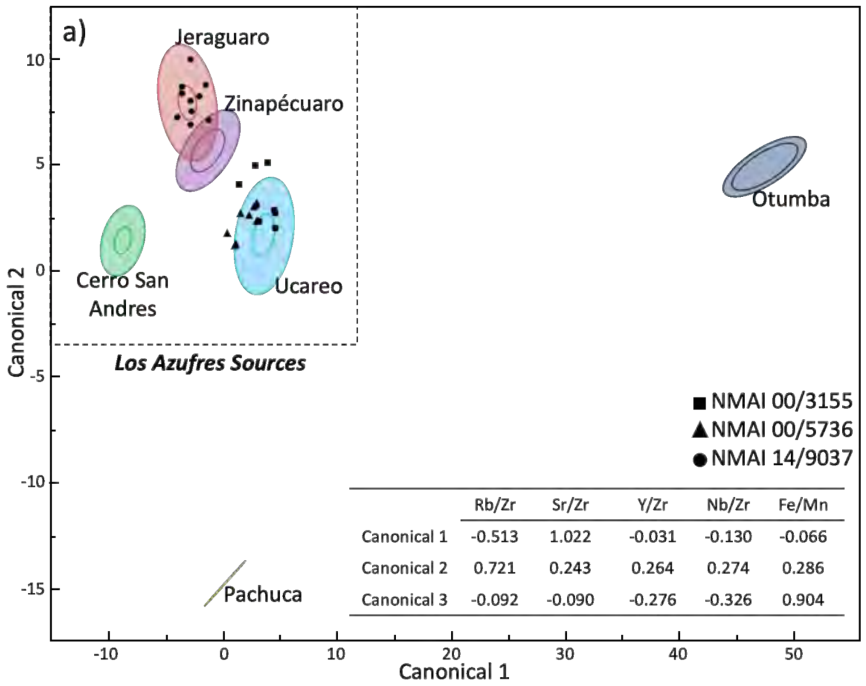




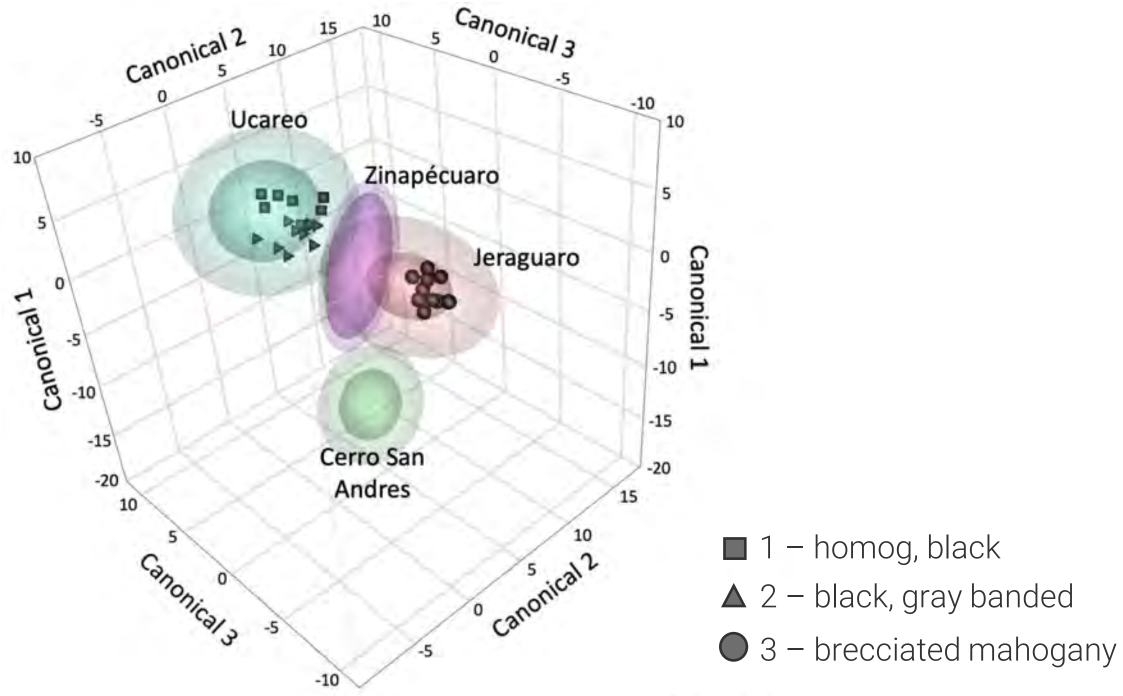
- Expected rhyolitic composition
  - Alkali elements separate Pachuca from other sources
  - Shows tablets are more closely related to the Los Azufres source
- Trace element ratios (Fe/Mn vs Rb/Sr) link
  - Samples 1 and 2 to the Ucareo source
  - Sample 3….

Sharps et al. (2021). Journal of Archaeological Science: Reports, 35, 102781

Example: Tandem analysis of large, Mesoamerican obsidian mirrors by SEM-based EDS and micro-XRF



	Rb/Zr	Sr/Zr	Y/Zr	Nb/Zr	Fe/Mn
Canonical 1	-0.513	1.022	-0.031	-0.130	-0.066
Canonical 2	0.721	0.243	0.264	0.274	0.286
Canonical 3	-0.092	-0.090	-0.276	-0.326	0.904



- Canonical discriminant analysis based on trace elements
  - Samples 1 and 2 confirmed to be related to the Ucareo source
  - Sample 3 aligns with Jeraguaro source compositions

Sharps et al. (2021). Journal of Archaeological Science: Reports, 35, 102781

Summary

- Scanning Electron Microscopy with new generation detectors and technologies allows data to accessed across scales easily
- Energy Dispersive Spectroscopic analysis can be applied across a range of applications in cultural heritage studies providing information down the smallest details but informing data interpretations across the workflow
- Flexible detector solutions mean implementation across almost any platform, from the most sophisticated instruments to benchtop solutions.

Questions, Thoughts or Comments?

If you have questions please **type your questions**, thoughts, or comments in the **Q&A box** and **press Submit**.

We ask for your understanding if we do not have time to discuss all comments and questions within the session. Any unanswered questions or comments will be answered and discussed by e-mail or in another Webex session.

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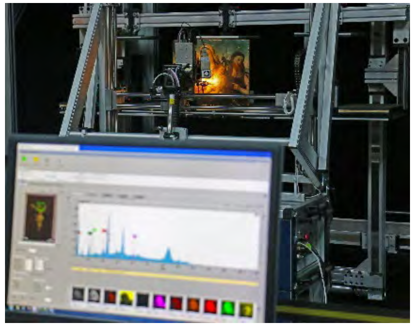

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