Elettra Sincrotrone Trieste

Synchrotron radiation for Cultural Heritage

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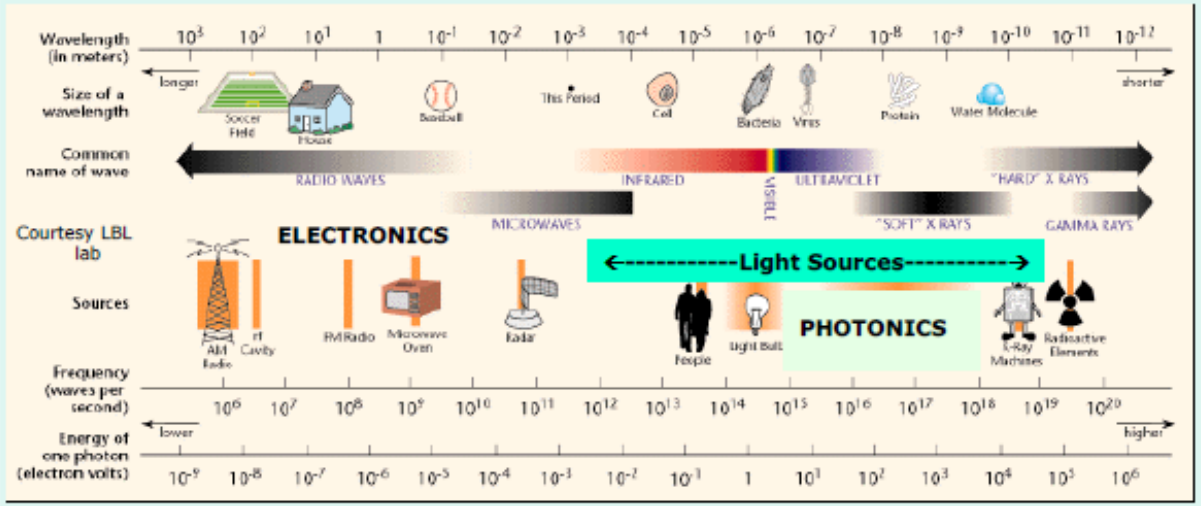
Synchrotron facilities for CH

- Synchrotrons are large facilities offering a plethora of advanced state-of-the art spectroscopic and imaging techniques ***for materials characterisation*** to be used by all scientific communities (and not only)
- They cover a broad radiation spectrum



Spectrum of Electromagnetic Radiation

Region	Wavelength (Angstroms)	Wavelength (centimetres)	Frequency (Hz)	Energy (eV)
Radio	$> 10^9$	> 10	$< 3 \times 10^9$	$< 10^{-5}$
Microwave	$10^9 - 10^6$	10 - 0.01	$3 \times 10^9 - 3 \times 10^{12}$	$10^{-5} - 0.01$
Infrared	$10^6 - 7000$	$0.01 - 7 \times 10^{-5}$	$3 \times 10^{12} - 4.3 \times 10^{14}$	0.01 - 2
Visible	7000 - 4000	$7 \times 10^{-5} - 4 \times 10^{-5}$	$4.3 \times 10^{14} - 7.5 \times 10^{14}$	2 - 3
Ultraviolet	4000 - 10	$4 \times 10^{-5} - 10^{-7}$	$7.5 \times 10^{14} - 3 \times 10^{17}$	$3 - 10^3$
X-Rays	10 - 0.1	$10^{-7} - 10^{-9}$	$3 \times 10^{17} - 3 \times 10^{19}$	$10^3 - 10^5$
Gamma Rays	< 0.1	$< 10^{-9}$	$> 3 \times 10^{19}$	$> 10^5$

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Synchrotron facilities for CH

- In the field of cultural heritage, integrated approaches combining different techniques are often required

- Synchrotron beamlines offer the possibility of performing different types of measurements at the same point of analysis, complementing preliminary information usually obtained by conventional laboratory and/or portable in situ methods

- In addition to accelerator and instrument upgrades currently and constantly on-going, the main challenges and improvements for scientific applications are focused on:

  (i) the use of combinations of complementary techniques at a single site;

  (ii) the joint use of several beamlines at the same facility

  (iii) the creation of a thematic network for accessing several facilities with a single proposal, also driven by new EU projects providing simultaneous access to multiple facilities (e.g., CERIC-ERIC, ReMAde@Ari, IPERION-CH/HS);

  (iv) the creation of new opportunities for improved experience in data analysis and data sharing (e.g., EXPANDS, PANOSC EU-funded projects)

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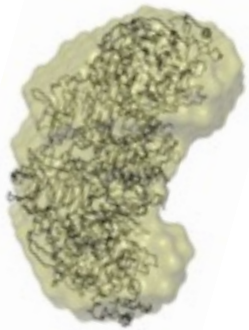
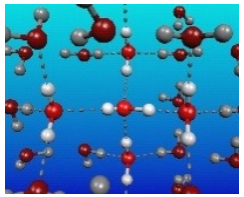
3rd Generation Synchrotron Light Source

X-ray Diffraction

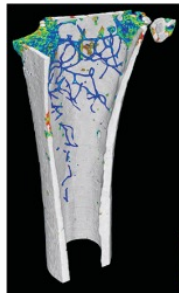
Small angle X-ray Scattering

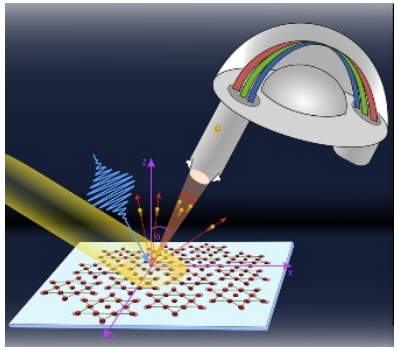




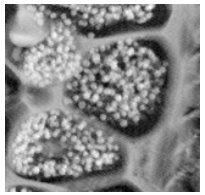
IR and Raman spectro-microscopies

X-ray μ-CT



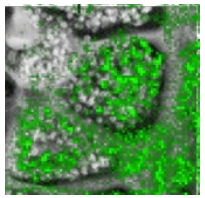


X-ray and UV Photoemission



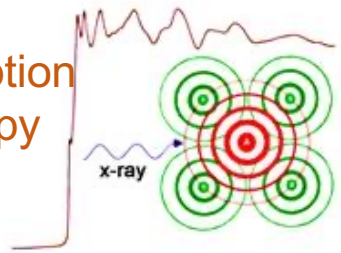
X-ray Microscopy

and



X-ray Fluorescence

X-ray Absorption Spectroscopy



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X-ray Fluorescence @ Synchrotrons

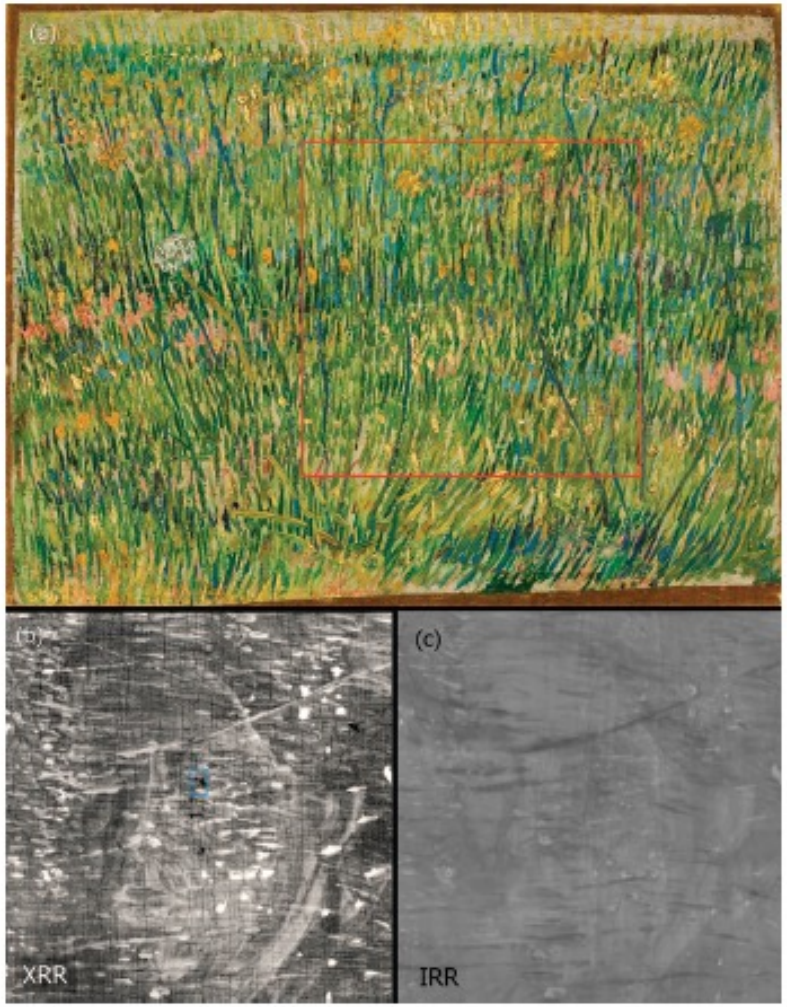
- Brilliant monochromatic X-ray source
- Focused X-ray beam: micrometric and nanometric scale
- State of the art manipulators for sample scanning

High chemical sensitivity
High spatial resolution

XRF microscopy

• Van Gogh (1853-1890) is one of the fathers of modern picture and was known for his vivid colors, the intense paint brushes dipinti and for his big productive career.

• His productivity is higher than we think since often he was re-utilising some older painting as base for a new painting.



Radiography IR Riflettography

Anal. Chem. **2008**, *80*, 6436–6442

Visualization of a Lost Painting by Vincent van Gogh Using Synchrotron Radiation Based X-ray Fluorescence Elemental Mapping

Joris Dik,*,† Koen Janssens,‡ Geert Van Der Snickt,‡ Luuk van der Loeff,§ Karen Rickers,∥ and Marine Cotte⊥,#

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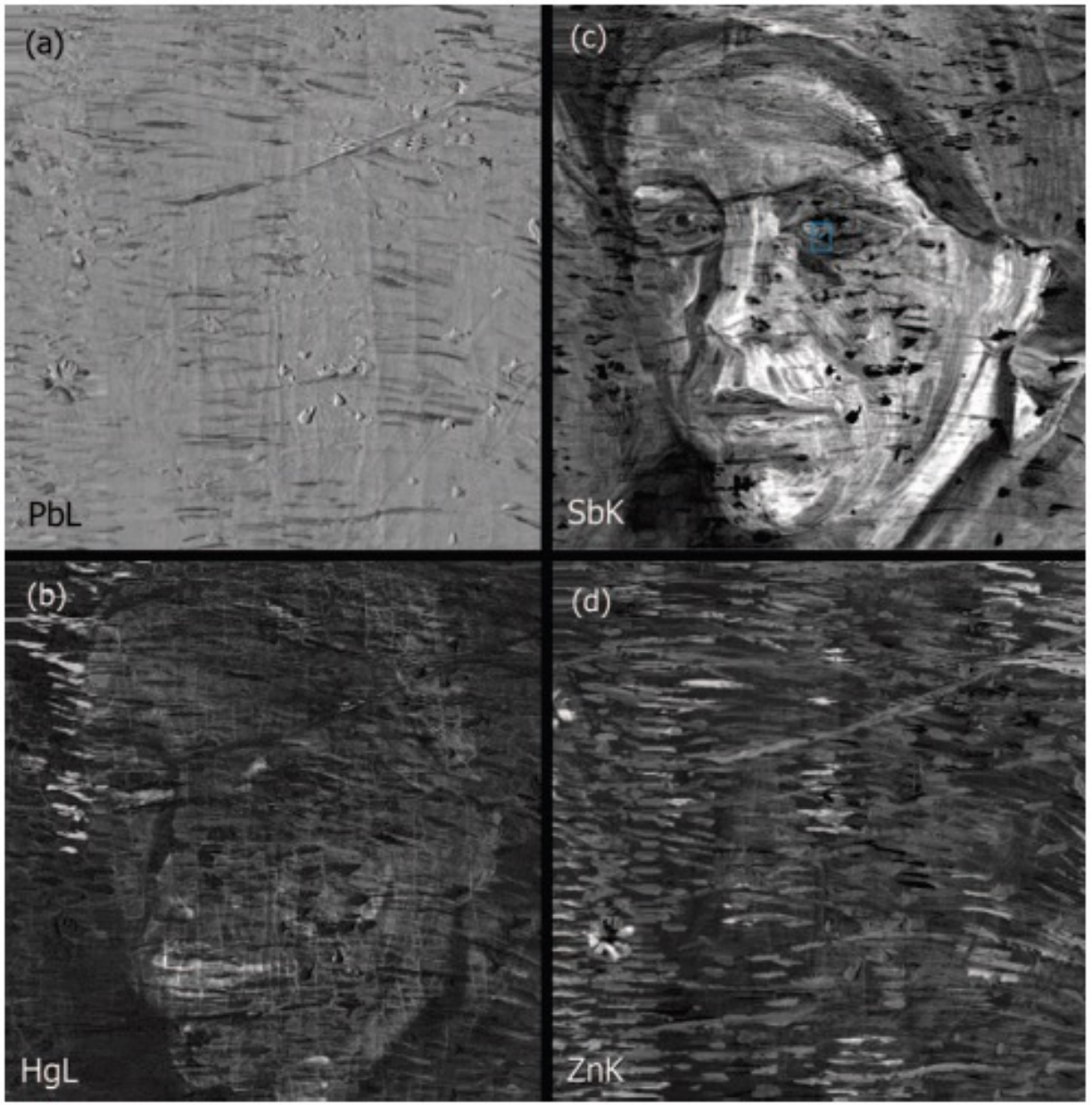
HASYLAB (Hamburg, Germany)

Beam (0.5 × 0.5 mm^2) at 38.5 keV

17.5 × 17.5 cm^2
dwell time: 2 s per pixel
total scan time ~ 2 days

The XRF scan revealed a number of elemental distributions that mostly correspond with the surface painting.
Its main elemental components include transition metals such as Mn, Cr, Co, Fe, Cu, Zn, As, and Ba.



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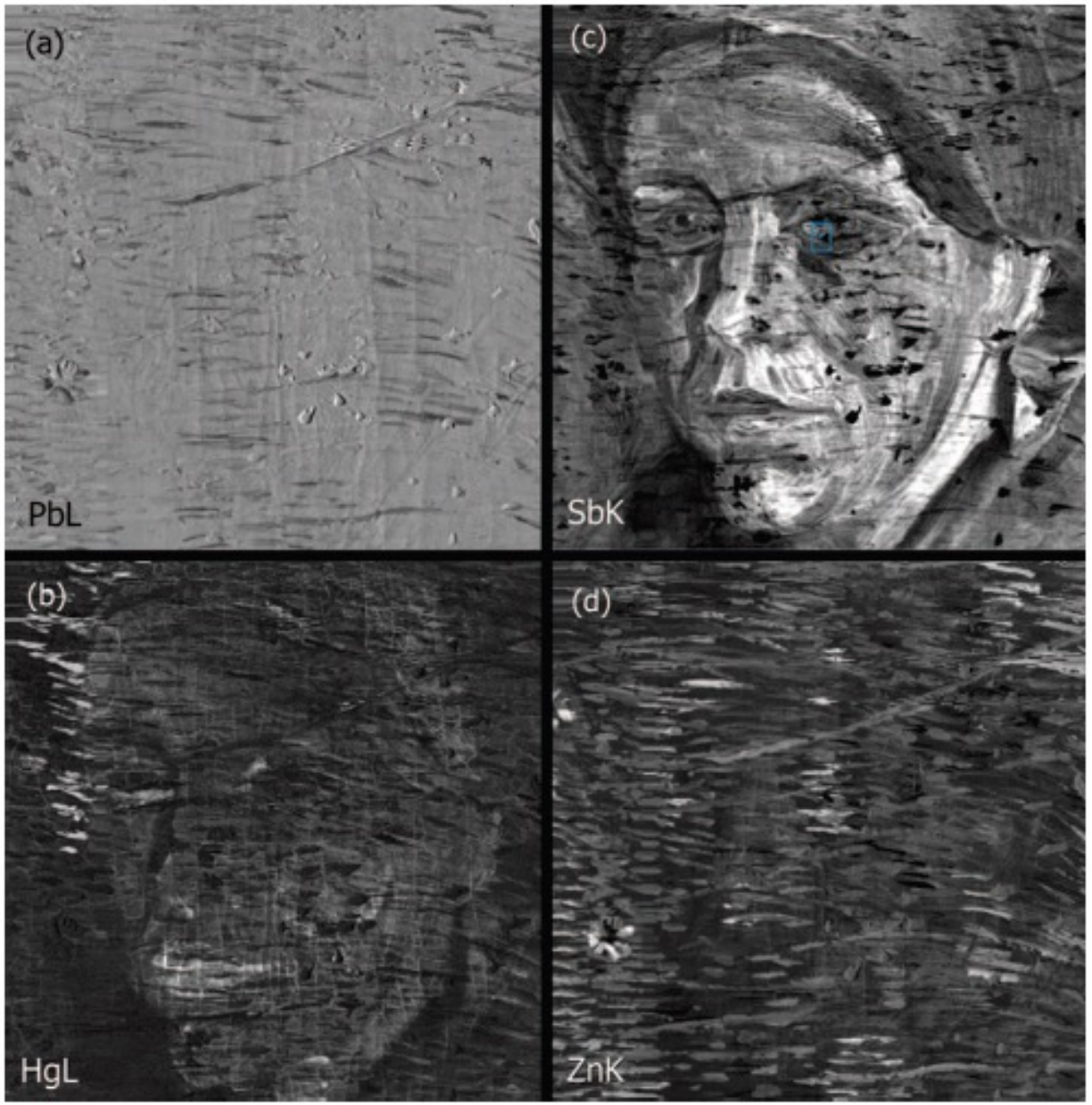

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(b) Detail from Head of a Woman, Nuenen, 1884-85, oil on canvas, 42 cm × 33 cm, Kröller-Müller Museum, Otterlo
(c) Detail from Head of a Woman, Nuenen, winter 1884-85, oil on canvas, 42 cm × 34 cm, Van Gogh Museum, Amsterdam.

J Dik et al. "Visualization of a Lost Painting by Vincent van Gogh Using Synchrotron Radiation Based X-ray Fluorescence Elemental Mapping" Anal. Chem. 2008, 80, 6436–6442

Conservation science: Ancient books

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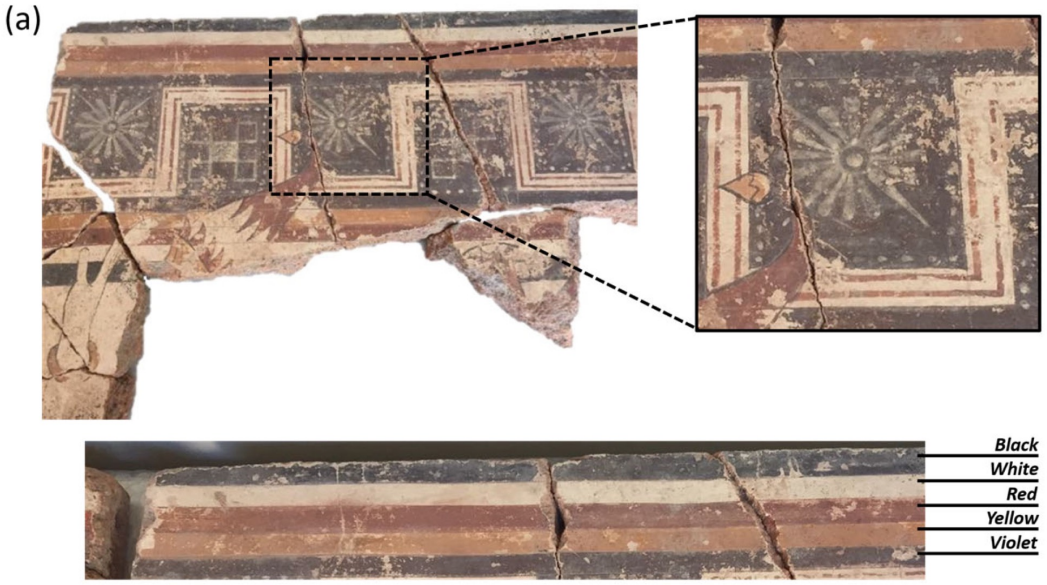
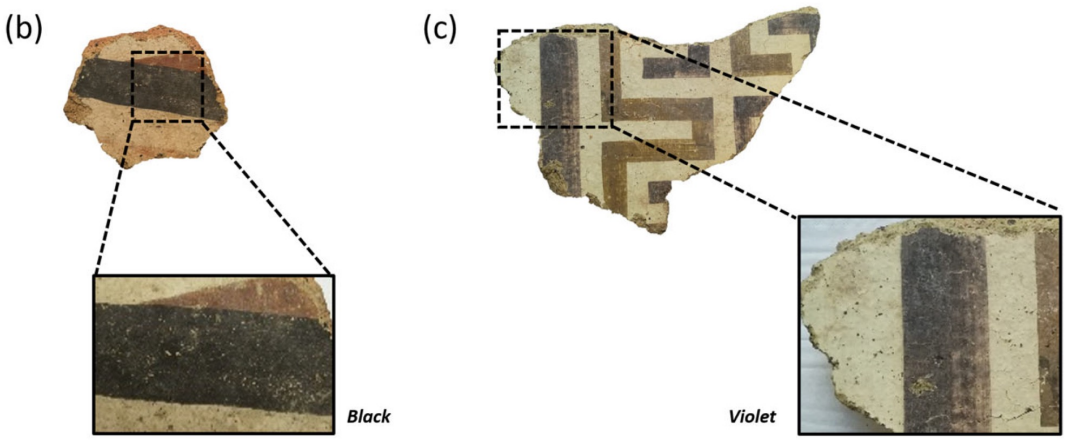
Painted terracotta from Cerveteri



Painted terracotta from Palatine Hill



The available literature on black decorations on Etruscan architectural terracottas carried out using routine laboratory or portable methods indicate the use of Fe- and Mn-based pigments

Different interpretations are proposed: the use of manganese-black technique or the use of natural pigments based on manganese and iron oxides

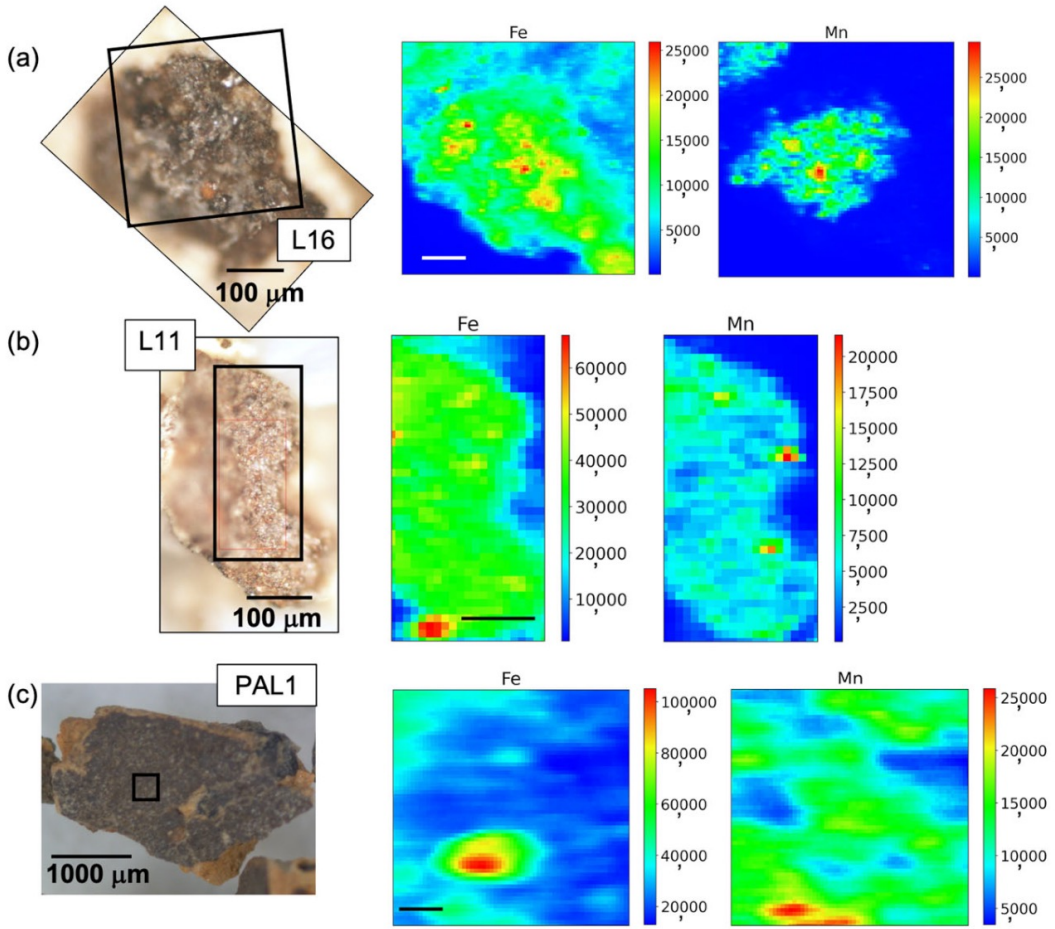
The advantage of the manganese black technique lies in the possibility of obtaining the red and black color in a single oxidizing firing cycle, starting from a mixture of Fe-Mn oxides (probably hematite and pyrolusite) that forms a stable spinel-like phase, namely, jacobsite ($MnFe_2O_4$).

Correctly characterizing or identifying manganese oxides by Raman spectroscopy can be complex

A. Gianoncelli et al. Heritage 2024, 7(4), 2118-2137; https://doi.org/10.3390/heritage7040100

Synchrotron – a plethora of techniques

XRF Microscopy @PUMA (SOLEIL)



Black pigments from Cerveteri and Palatine Hill

In the majority of the samples, manganese, present in the pigment layer, seems to be localized on the colored surface together with iron, which mainly comes from the background

On some spots pertaining to the pigment layers, Fe-Mn colocalization can be observed.

A. Gianoncelli et al. Heritage 2024, 7(4), 2118-2137; https://doi.org/10.3390/heritage7040100

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Synchrotron – a plethora of techniques

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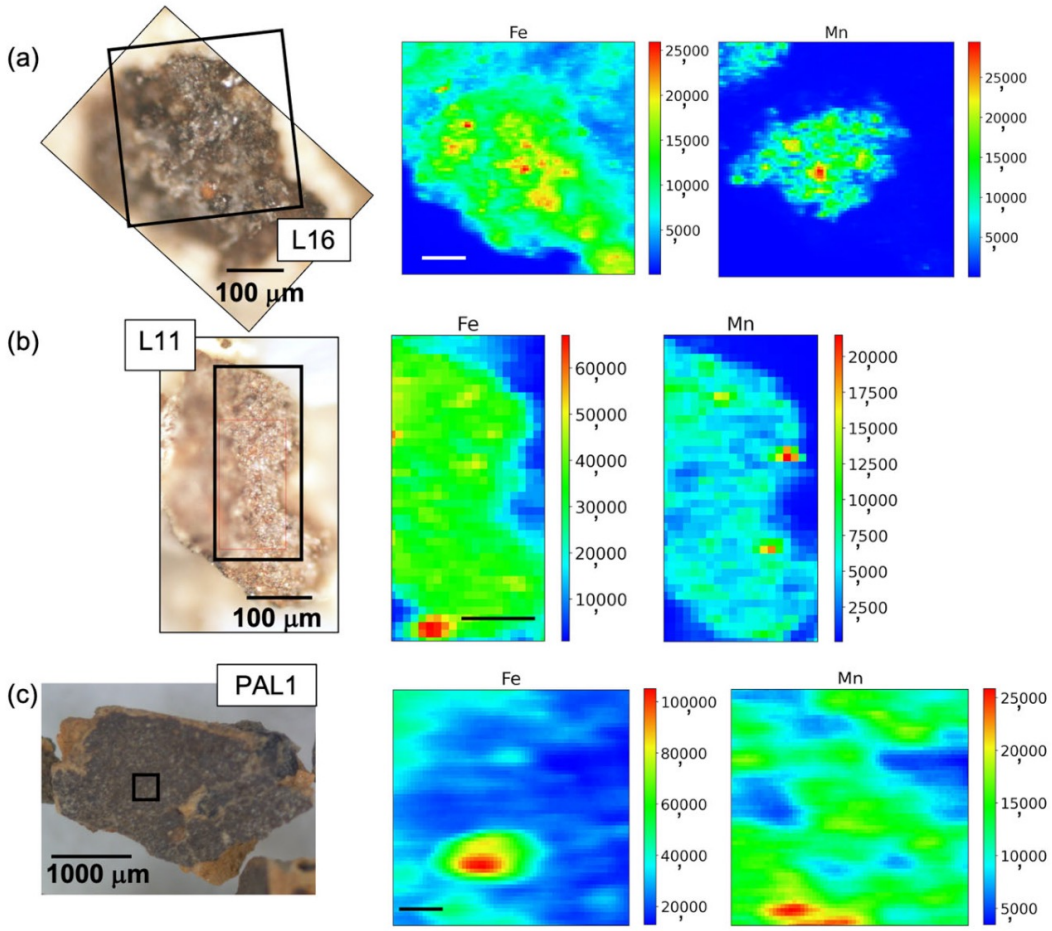
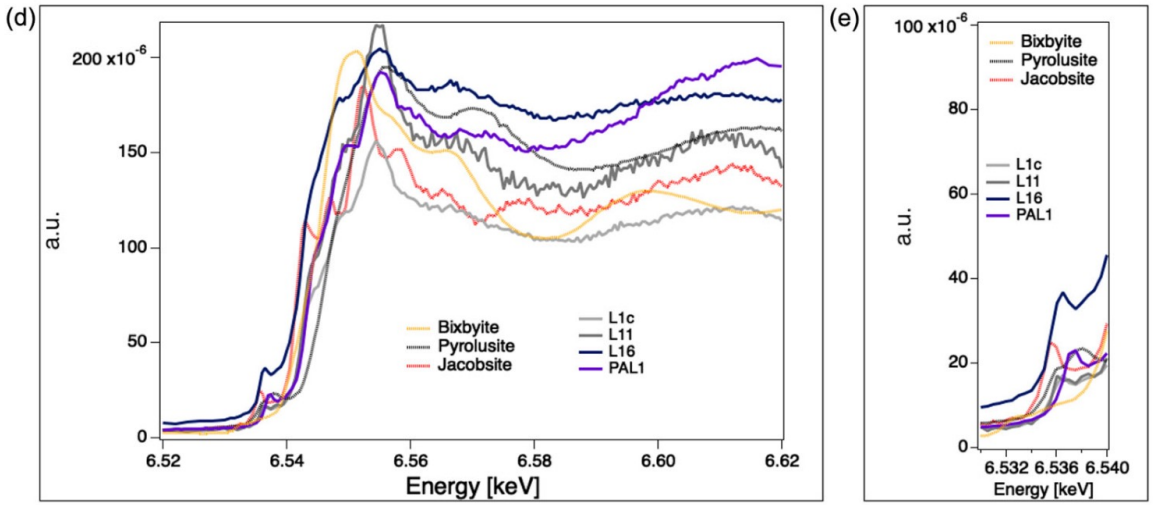


Black pigments from Cerveteri and Palatine Hill

XANES Spectroscopy @PUMA (SOLEIL)



The pre-edge structure appears to correspond to hausmannite or jacobsite (e.g., Pal1 and L16), while the edge position and post-edge features are more closely related to pyrolusite

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Synchrotron – a plethora of techniques

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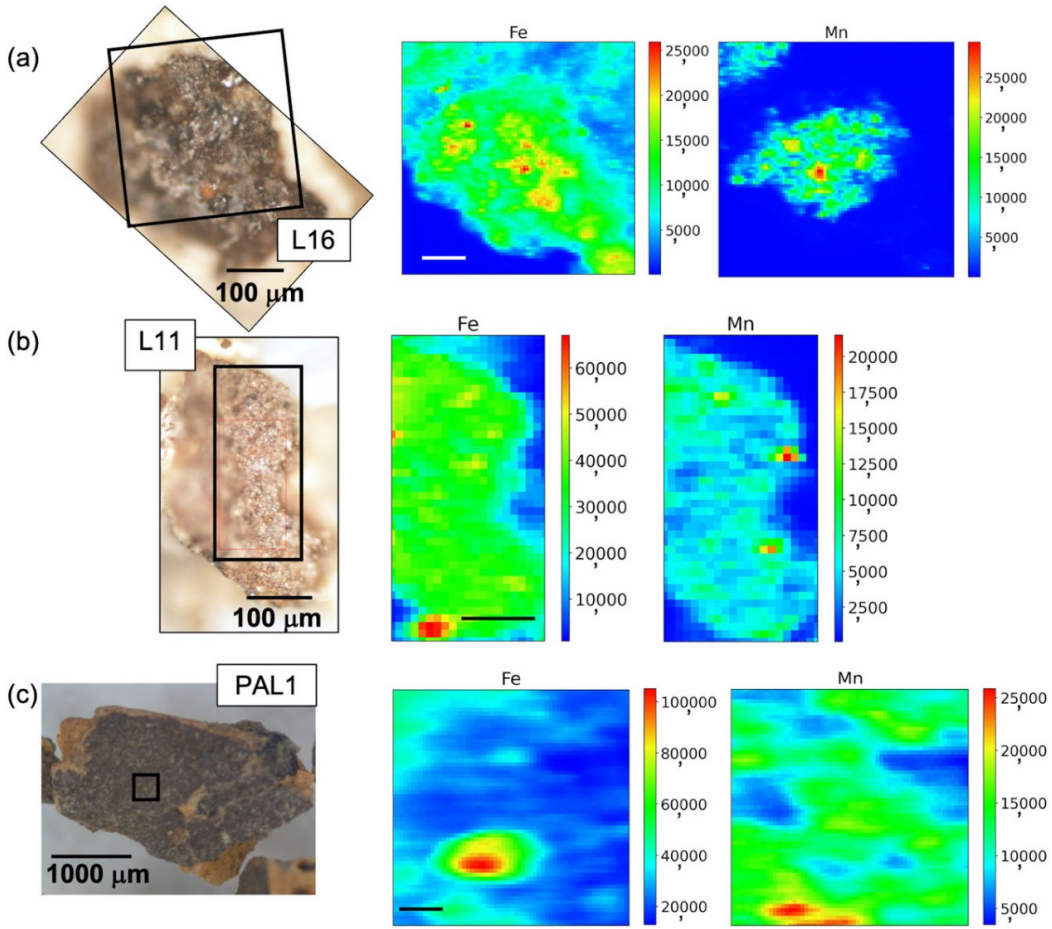
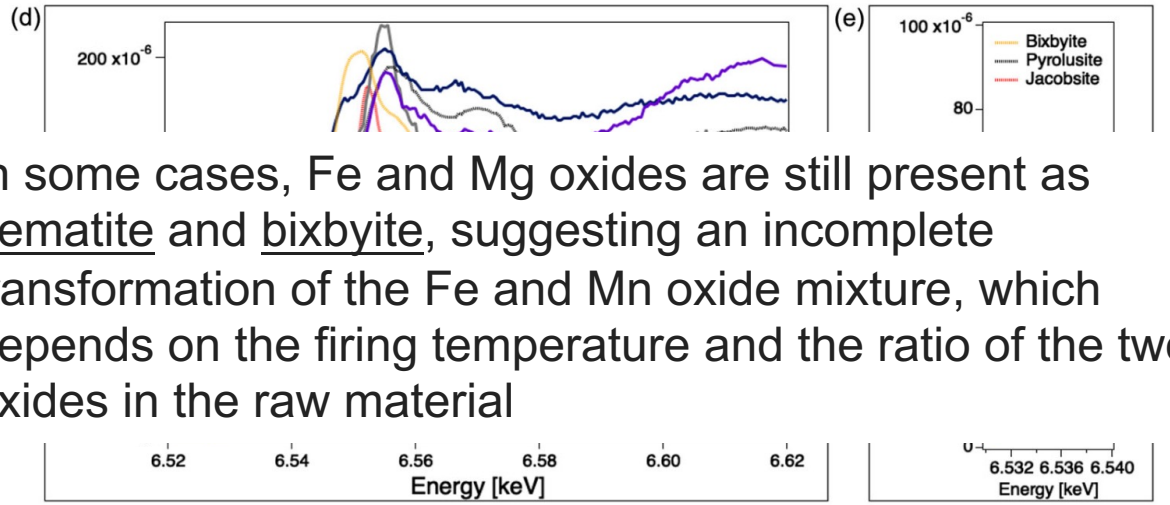


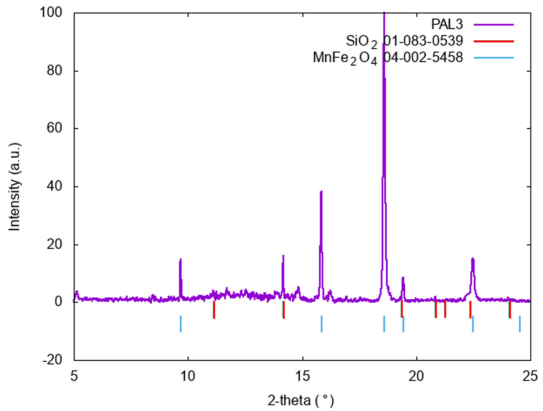
Black pigments from Cerveteri and Palatine Hill

XANES Spectroscopy @PUMA (SOLEIL)



In some cases, Fe and Mg oxides are still present as hematite and bixbyite, suggesting an incomplete transformation of the Fe and Mn oxide mixture, which depends on the firing temperature and the ratio of the two oxides in the raw material

X-ray diffraction @MCX (Elettra)



Sample ID	Mineralogical Phases (in Order of Relative Abundance)
L1c	Quartz, anorthite (Na-bearing, disordered), melilite, **Mn-Fe spinel (jacobsite; $[MnFe]_2O_4$)**, clay minerals (illite, ?).
L9	Quartz, anorthite (Na-bearing), hematite, **Mn-Fe spinel (jacobsite; $[MnFe]_2O_4$)**, bixbyite (Mn_2O_3).
Pal1	Quartz, **Mn-Fe spinel (jacobsite; $[MnFe]_2O_4$)**.
Pal3	**Mn-Fe spinel (jacobsite; $[MnFe]_2O_4$)**, quartz.
Pal13	Quartz, calcite, Fe-Mn spinel **(jacobsite; $[MnFe]_2O_4$)**, gehlenite.

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Archaeological excavations carried out during 1977 in Saturo (10 km South-East of Taranto, Italy) have disclosed a sanctuary in use since the 7th century B.C.
Over one thousand silver silver coins and two gold ones were found, in addition to some precious golden artefacts

Due to the high oxygenation, humidity and chloride concentration, a notable fraction of the retrieved silver coins exhibits **heavy encrustations** overlying the original metal volume

The historical and artistic importance of these items calls for material protection and restoration.

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Focus article

Electrochemical reconstruction of a heavily corroded Tarentum hemiobolus silver coin: a study based on microfocus X-ray computed microtomography

Benedetto Bozzini [a, *], Alessandra Gianoncelli [b], Claudio Mele [a], Aldo Siciliano [c], Lucia Mancini [b]

[a] Dipartimento di Ingegneria dell'Innovazione, Università del Salento, Via Monteroni, 73100 Lecce, Italy
[b] Elettra – Sincrotrone Trieste S.C.p.A., S.S. 14-km 163.5 in Area Science Park, 34149 Basovizza, Trieste, Italy
[c] Dipartimento di Beni Culturali, Università del Salento, Via Dalmazio Birago 64, 73100 Lecce, Italy

Hemiobolus minted in Taranto dated ca. 280 B.C

Thick corrosion layers on both sides, hiding almost completely the original engraving.
Severely embrittled and typically with open cracks filled with corrosion products.

The coin exhibited two crescents and four pellets on the obverse side and two crescents, pellets and "*Λl*" inscription on the reverse one.

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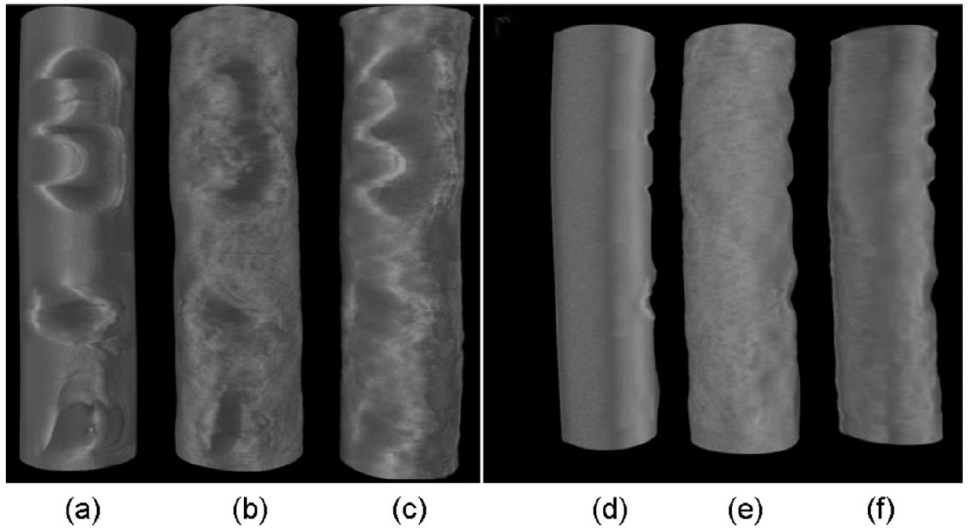

Fig. 4. Volume renderings obtained by X-ray mCT of: (a, d) original (2 mm diameter), (b, e) corroded and (c, f) reduced Ag wire sample. Panels (a)–(c) show frontal views of the engraved numbers, panels (d)–(e) depict side views.

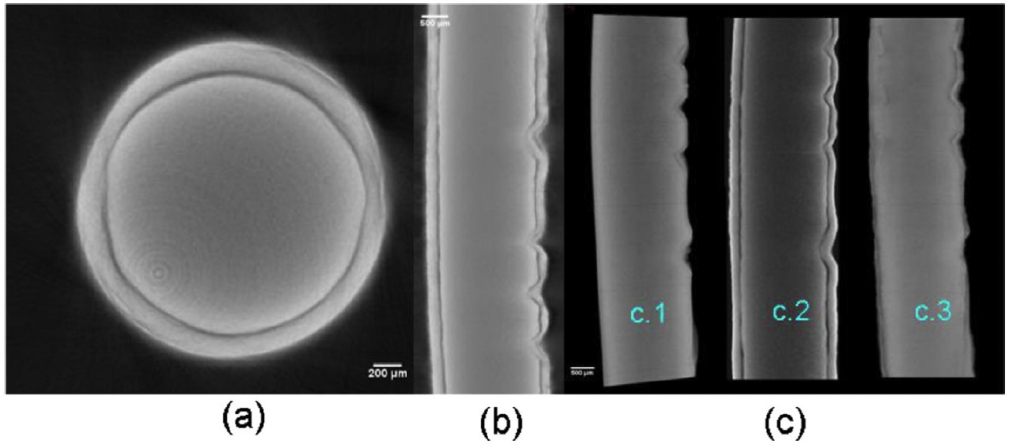

Fig. 5. Virtual sections, obtained by X-ray mCT, of the Ag wire: (a) XY (axial slice) of the Ag wire in corroded conditions; (b) higher magnification of the ZY plane of the Ag wire in corroded conditions (compare with Panel (c.2)); (c) ZY planes of pristine (c.1), corroded (c.2) and reduced (c.3) sample.

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We studied the controlled corrosion and reduction of engraved Ag wires.

We formed a thick AgCl layer and in the subsequent cathodic treatment we reduced the adherent AgCl layer back to metallic Ag.

We selected operating conditions ensuring the formation of thick (several tens of um), adherent AgCl layers, like the ones found in the heavily corroded ancient Ag coins.

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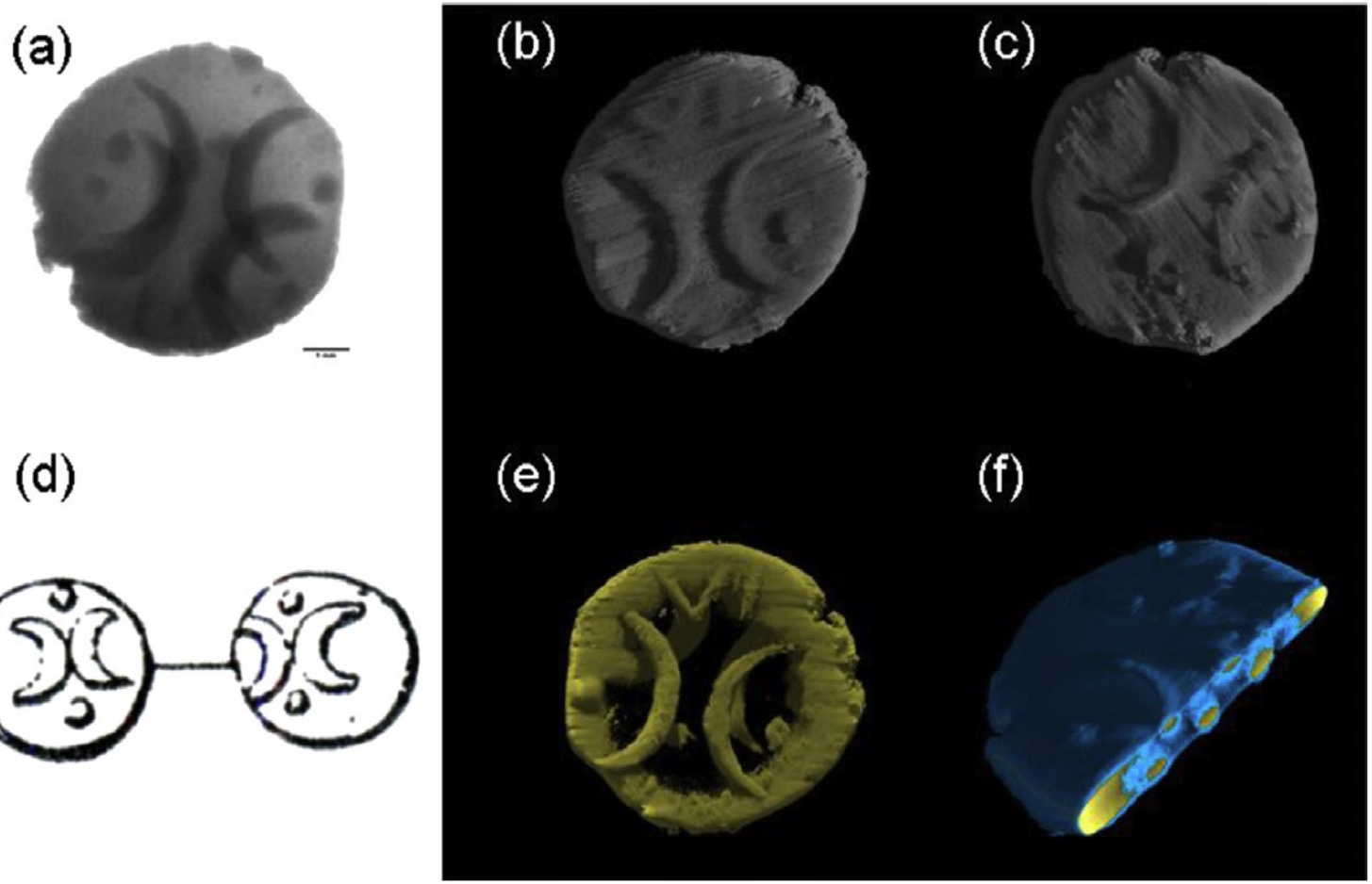
MicroCT rendering

Microradiograph

Rendering



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Volume renderings obtained by X-ray mCT of the pristine and of the restored coin

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Summary and challenges

- X-ray spectro-microscopy techniques have proven to be a valuable tool for exploring complex matter at sub-micrometric level
- Multimodal imaging often available at synchrotrons
- X-ray-based techniques are only a part of the possibilities offered by synchrotron sources for the study of CH materials. In fact, other synchrotron-radiation-based techniques such as Fourier-transform infrared (FTIR) and Raman spectroscopies provide complementary information
- Correlative research is essential (FTIR, PIXE, EM, lab-related bulk analysis & others)
- A limited number of samples can be analysed due to the relatively difficult access to synchrotron facilities
- Radiation damage

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