X-ray Absorption Spectroscopy: a versatile technique

Laura Simonelli
CLÆSS beamline responsible

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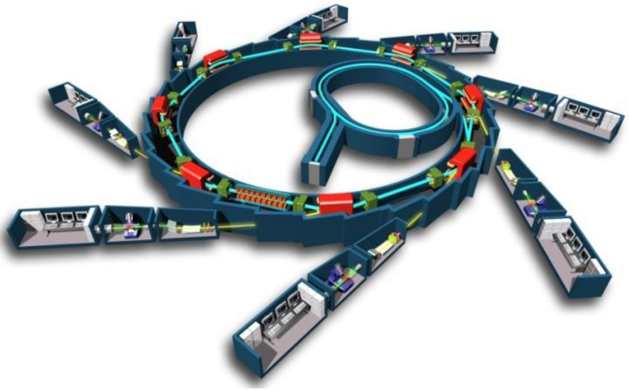
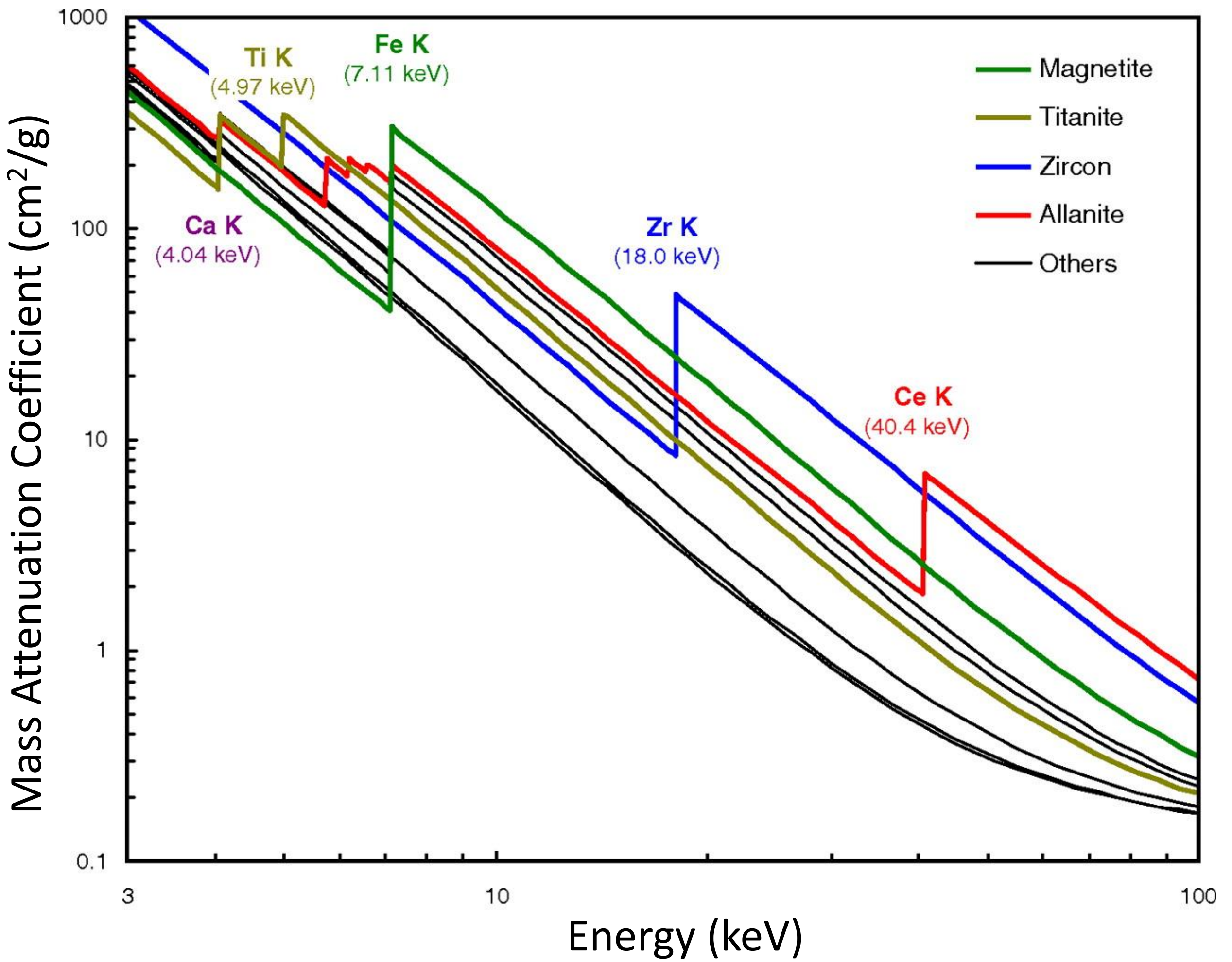
Photon absorption



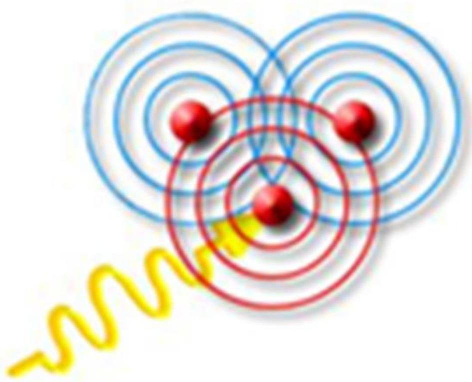
The synchrotron radiation interacts with the electrons bound in an atom.

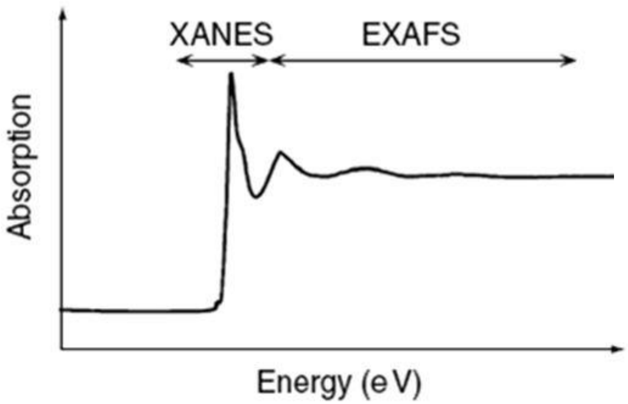
Scattered radiation

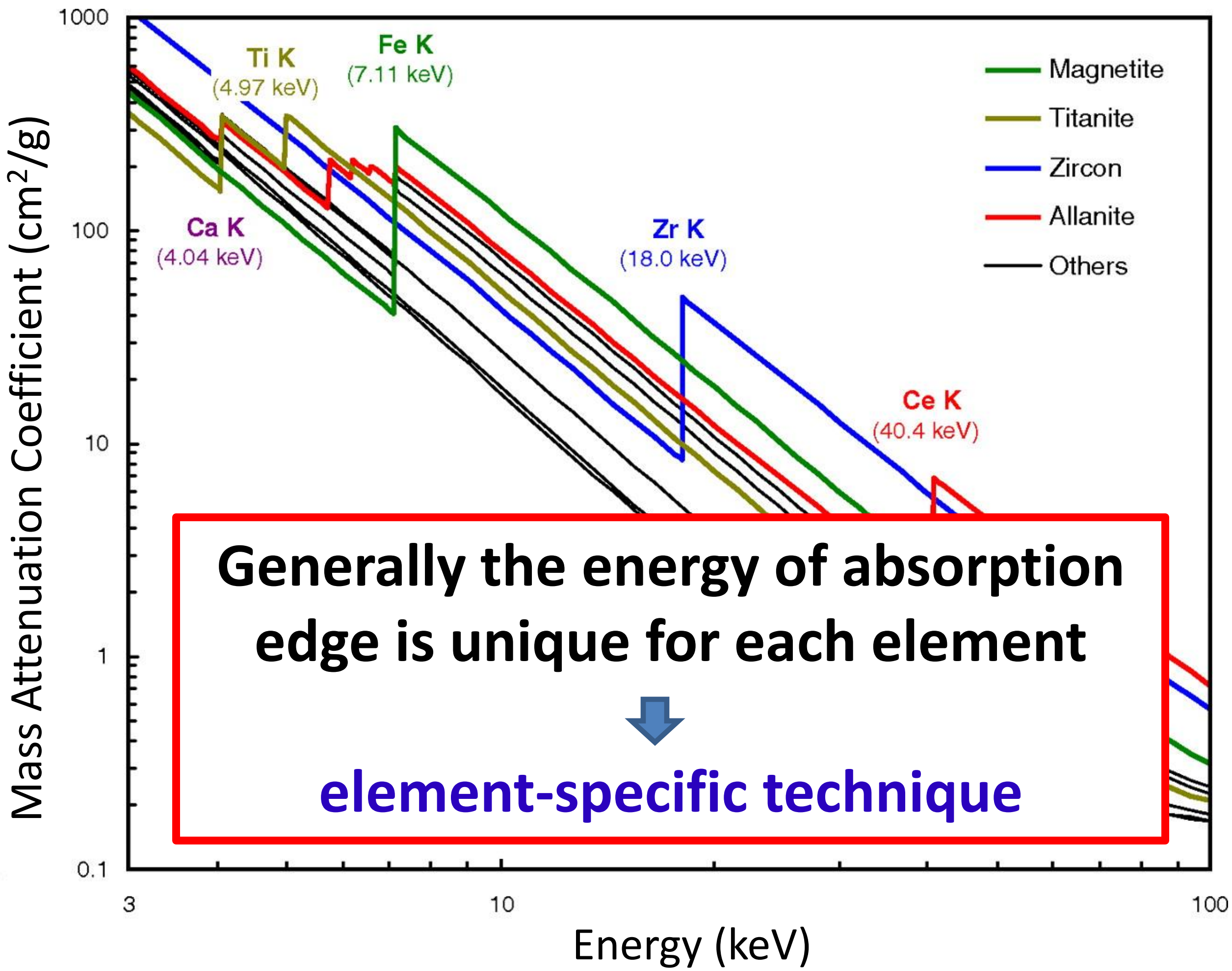
Absorbed radiation



X-ray absorption spectroscopy (XAS)







Generally the energy of absorption edge is unique for each element

element-specific technique

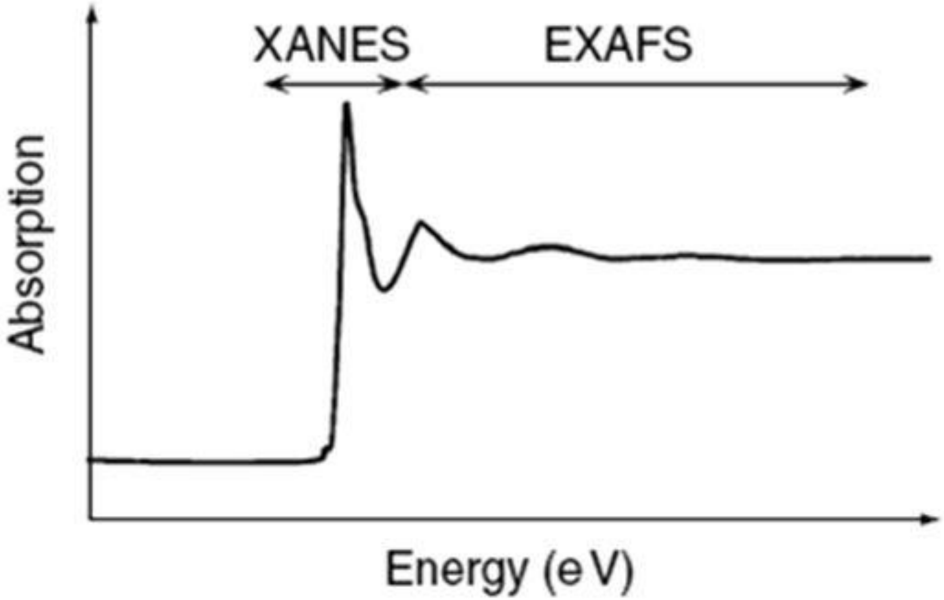
XAS: complementary information

XANES

- Oxidation state
- Unoccupied electronic states
- Spin state
- Local structure
- direct information about bond angles.

EXAFS

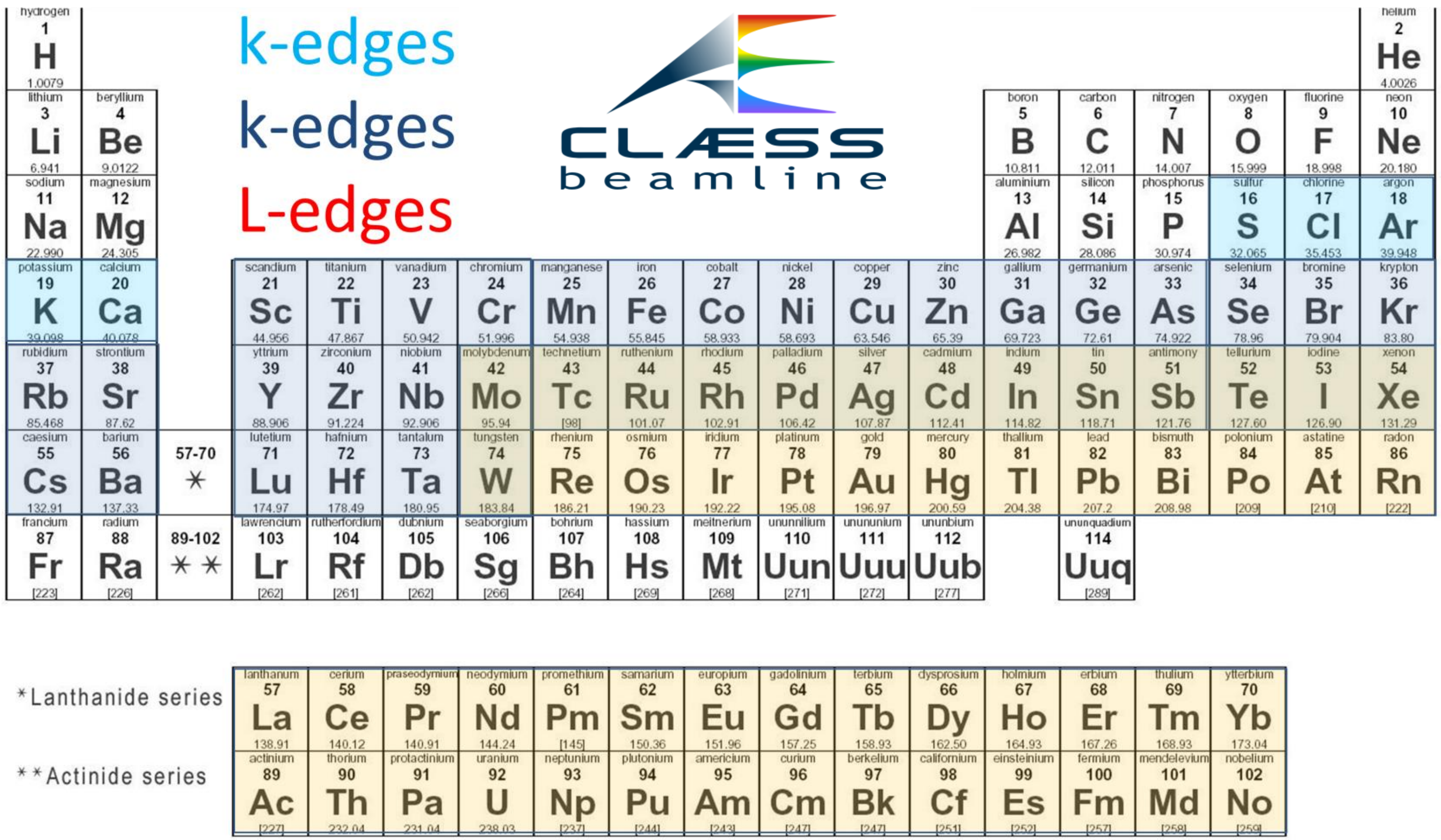
- Bond distances
- Coordination number
- Static and dynamic disorder



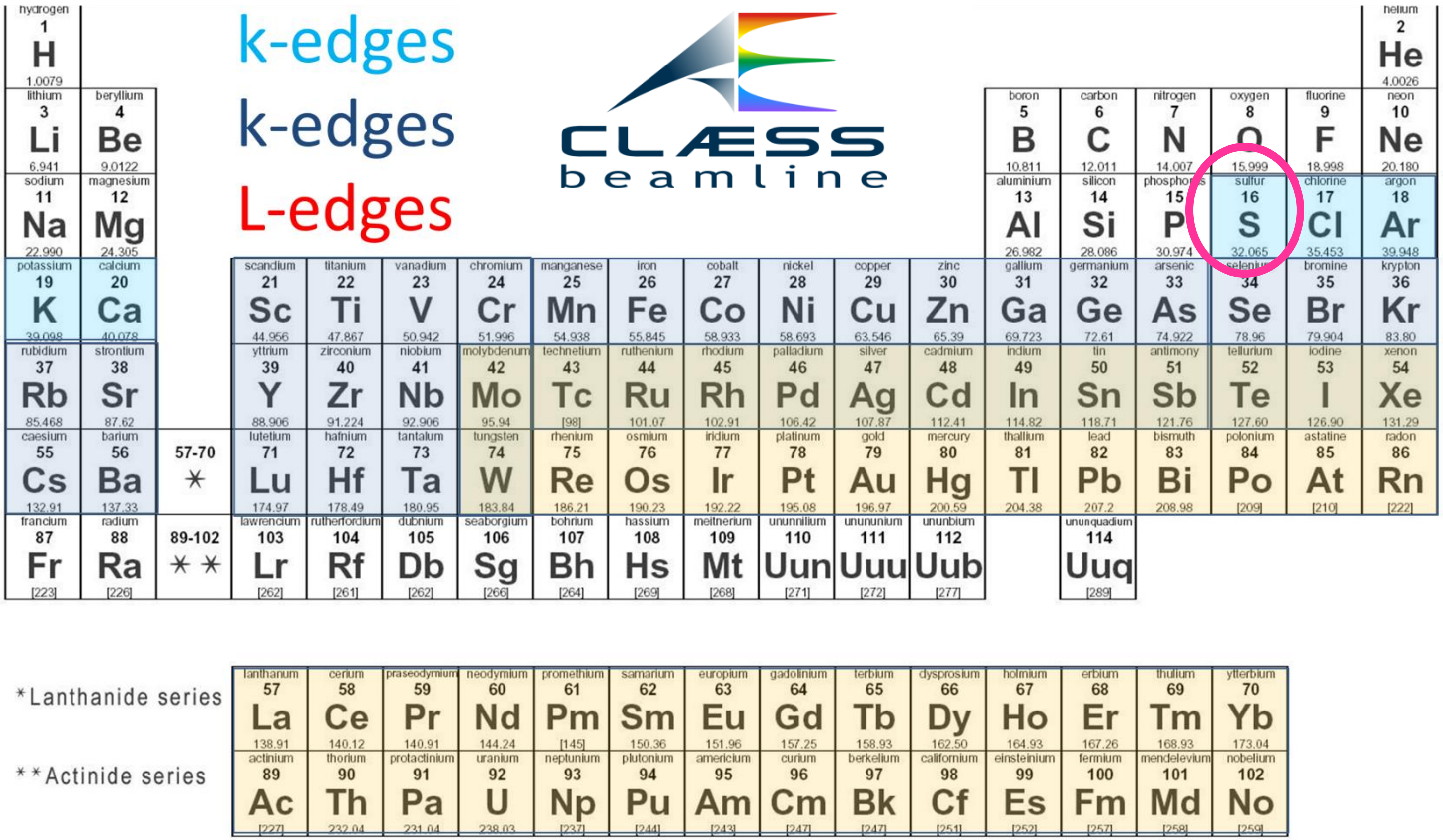
Which materials can be investigated by XAS?

XAS is an element sensitive local probe that can be applied to any kind of materials: Crystals, glass, liquids, etc…

CLÆSS energy range: 2.4 – 62.3 keV



CLÆSS energy range: 2.4 – 62.3 keV



ALBA

analytical chemistry

Article

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Combined use of Synchrotron Radiation Based Micro-X-ray Fluorescence, Micro-X-ray Diffraction, Micro-X-ray Absorption Near-Edge, and Micro-Fourier Transform Infrared Spectroscopies for Revealing an Alternative Degradation Pathway of the Pigment Cadmium Yellow in a Painting by Van Gogh

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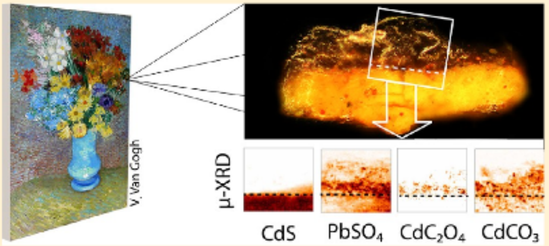
ABSTRACT: Over the past years a number of studies have described the instability of the pigment cadmium yellow (CdS). In a previous paper we have shown how cadmium sulfide on paintings by James Ensor oxidizes to $CdSO_4 \cdot H_2O$. The degradation process gives rise to the fading of the bright yellow color and the formation of disfiguring white crystals that are present on the paint surface in approximately 50 μm sized globular agglomerations. Here, we study cadmium yellow in the painting "Flowers in a blue vase" by Vincent van Gogh. This painting differs from the Ensor case in the fact that (a) a



Time instability of the pigment cadmium yellow (CdS)

Experimental approach

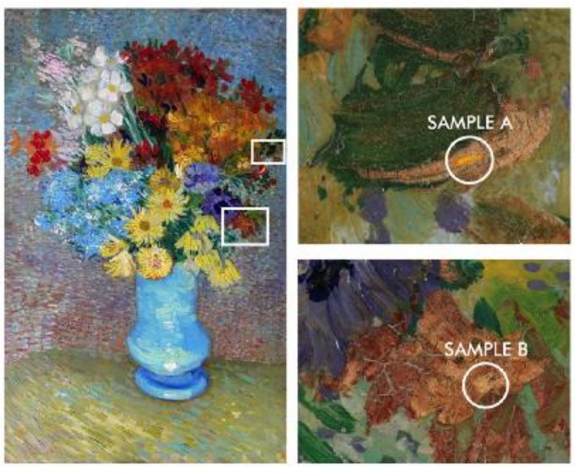
µ-XRD

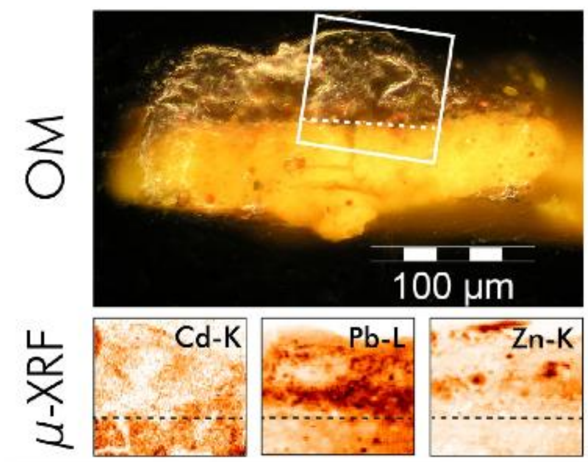
µ-XANES

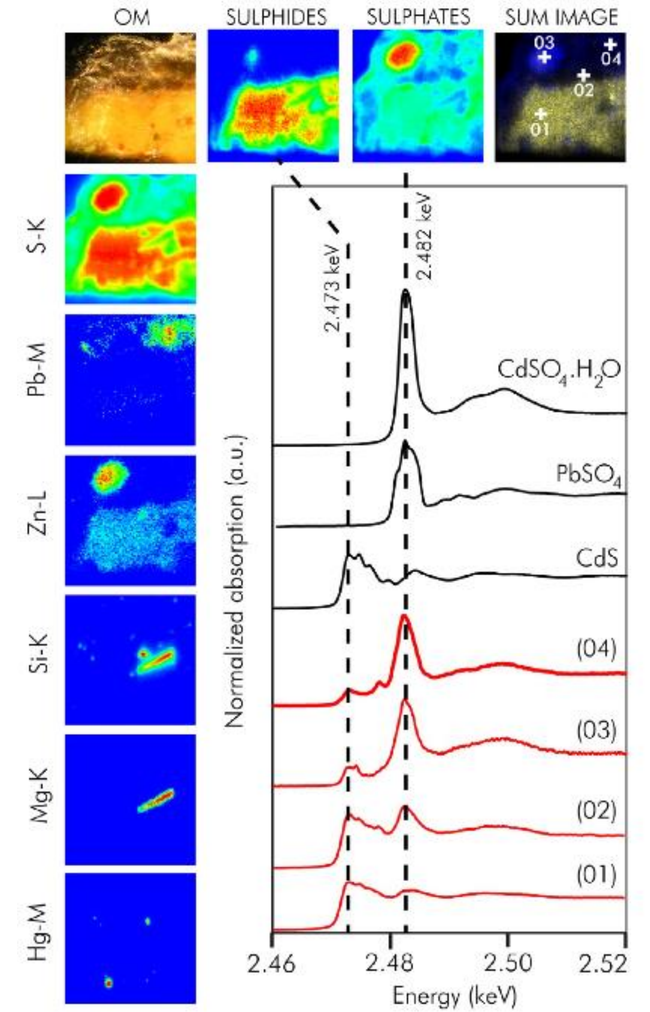
µ-XRF

µ-FT-IR

No crystalline $CdSO_4$ compounds were identified on the Van Gogh paint samples → the observed degradation was initially caused by oxidation of the original CdS Pigment

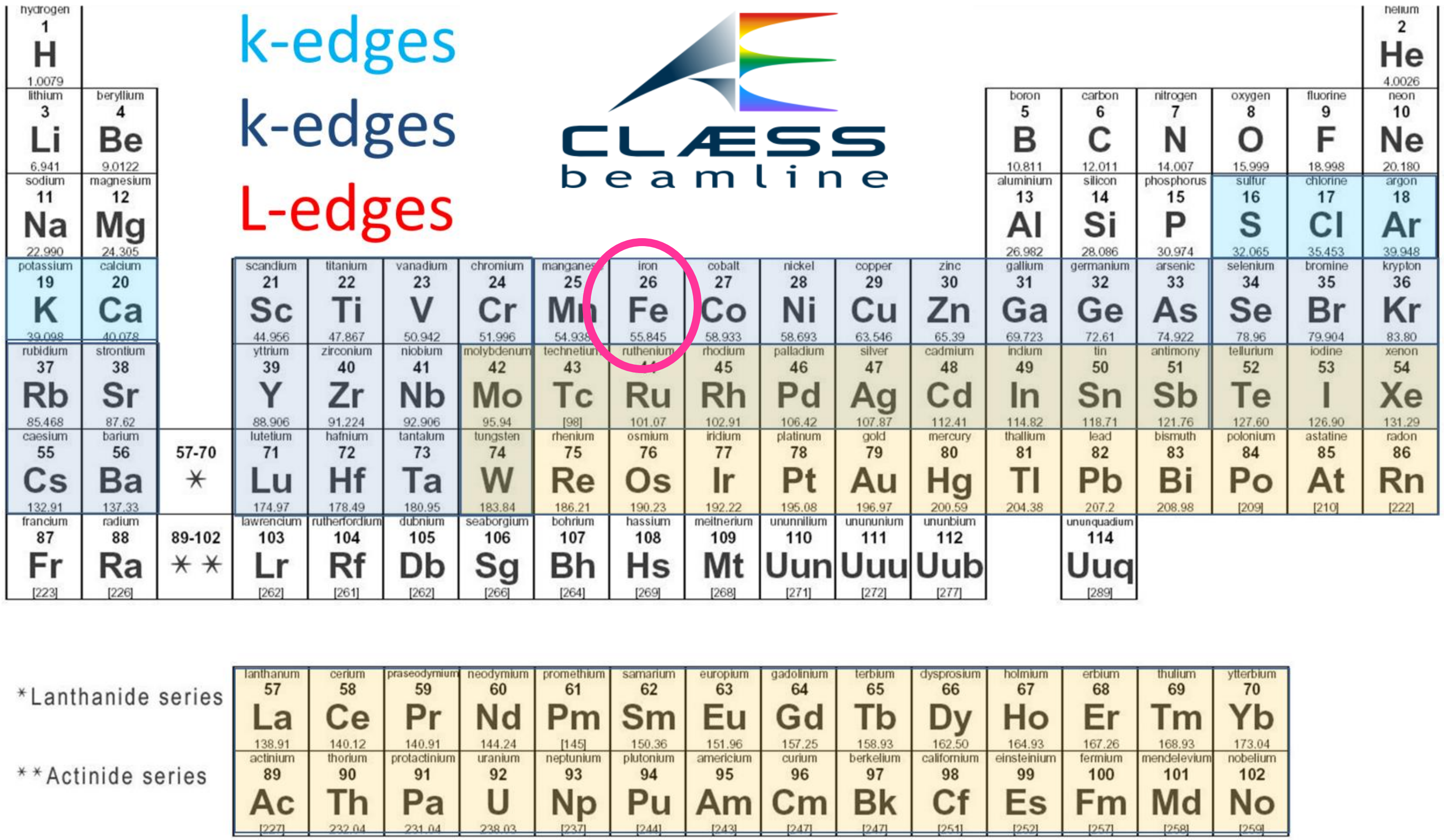


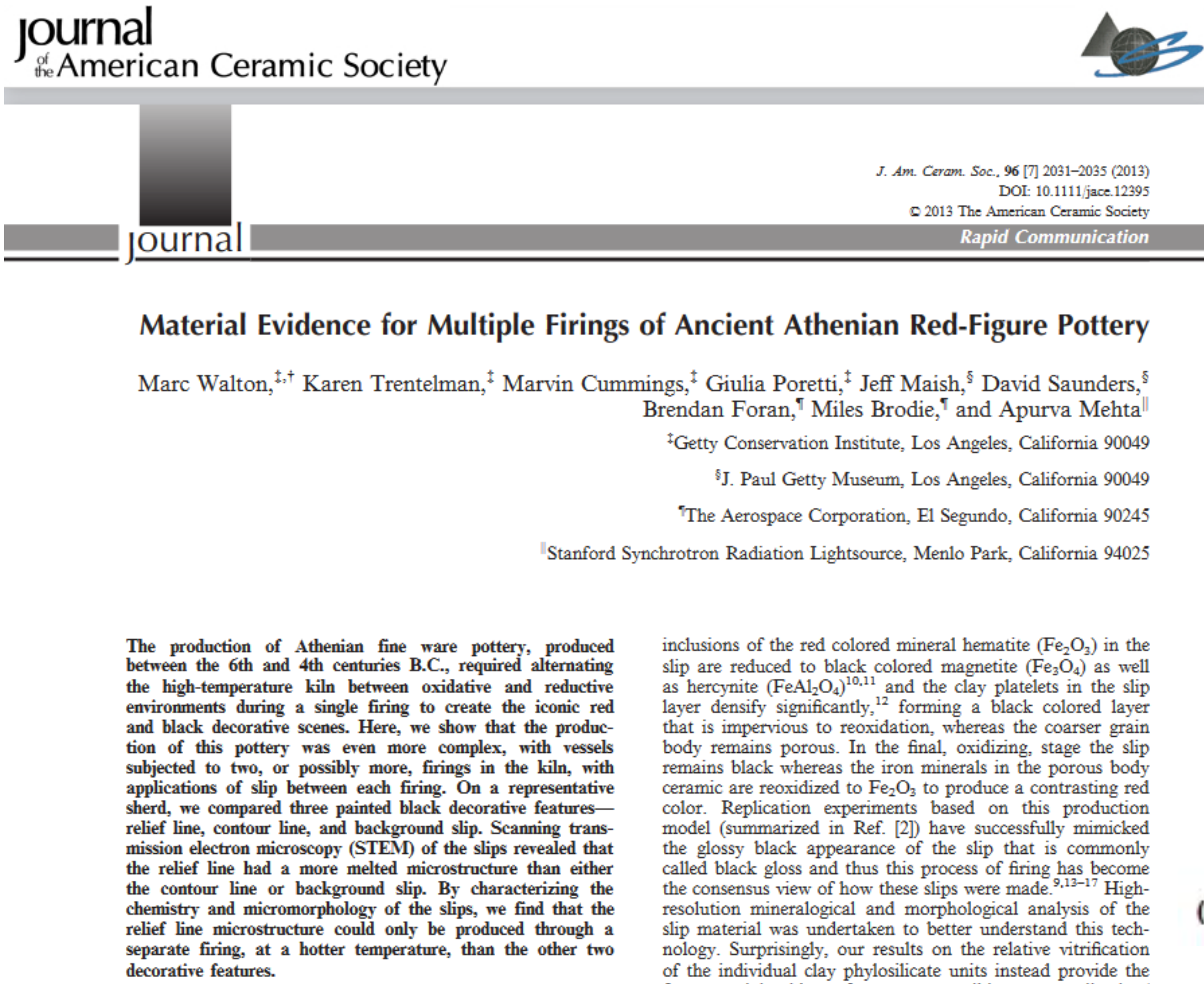




The resulting opaque anglesite compound in the varnish, in combination with the underlying CdC_2O_4 layer at the paint/varnish interface, account for the orange-gray crust that is disfiguring the painting on a macroscopic level.

CLÆSS energy range: 2.4 – 62.3 keV





Journal of the American Ceramic Society

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journal
Rapid Communication

Material Evidence for Multiple Firings of Ancient Athenian Red-Figure Pottery

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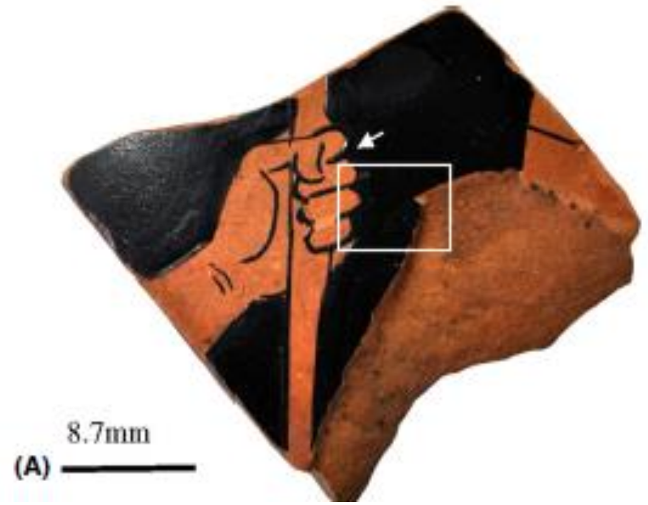
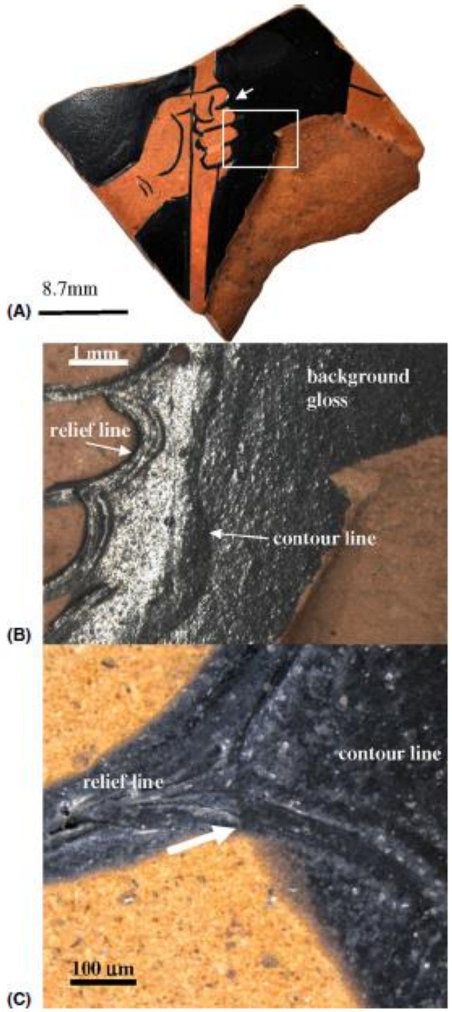
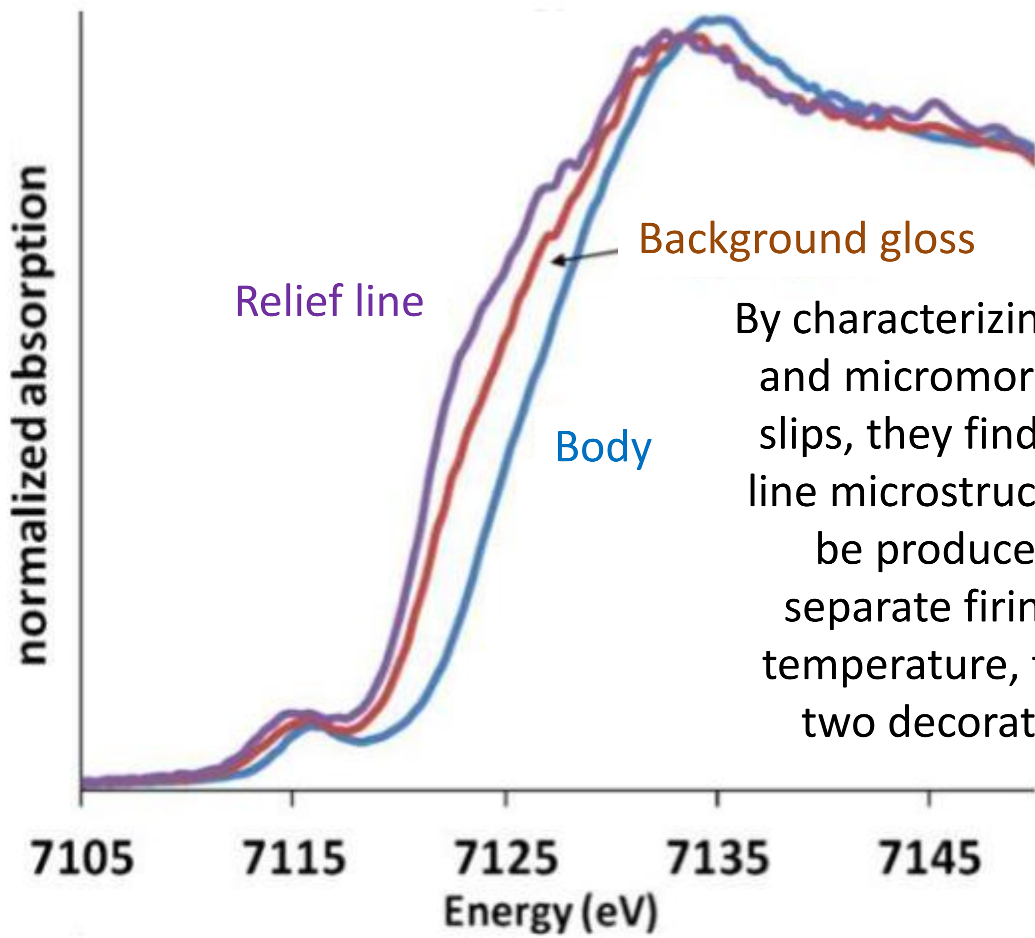
The production of Athenian fine ware pottery, produced between the 6th and 4th centuries B.C., required alternating the high-temperature kiln between oxidative and reductive environments during a single firing to create the iconic red and black decorative scenes. Here, we show that the production of this pottery was even more complex, with vessels subjected to two, or possibly more, firings in the kiln, with applications of slip between each firing. On a representative sherd, we compared three painted black decorative features—relief line, contour line, and background slip. Scanning transmission electron microscopy (STEM) of the slips revealed that the relief line had a more melted microstructure than either the contour line or background slip. By characterizing the chemistry and micromorphology of the slips, we find that the relief line microstructure could only be produced through a separate firing, at a hotter temperature, than the other two decorative features.

inclusions of the red colored mineral hematite (Fe_2O_3) in the slip are reduced to black colored magnetite (Fe_3O_4) as well as hercynite ($FeAl_2O_4$)[10,11] and the clay platelets in the slip layer densify significantly,[12] forming a black colored layer that is impervious to reoxidation, whereas the coarser grain body remains porous. In the final, oxidizing, stage the slip remains black whereas the iron minerals in the porous body ceramic are reoxidized to Fe_2O_3 to produce a contrasting red color. Replication experiments based on this production model (summarized in Ref. [2]) have successfully mimicked the glossy black appearance of the slip that is commonly called black gloss and thus this process of firing has become the consensus view of how these slips were made.[9,13–17] High-resolution mineralogical and morphological analysis of the slip material was undertaken to better understand this technology. Surprisingly, our results on the relative vitrification of the individual clay phylosilicate units instead provide the

Several high temperature treatments between oxidative and reductive environments to create the red and black decorative scenes







By characterizing the chemistry and micromorphology of the slips, they find that the relief line microstructure could only be produced through a separate firing, at a hotter temperature, than the other two decorative features.

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analytical chemistry
Article
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Confocal XANES and the Attic Black Glaze: The Three-Stage Firing Process through Modern Reproduction

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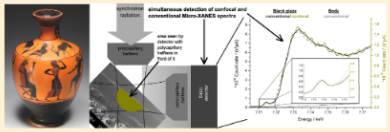
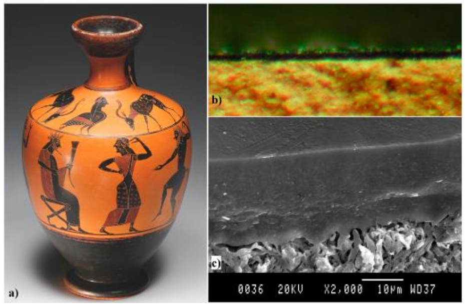
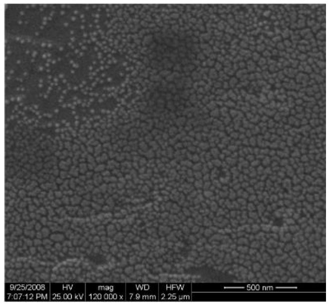
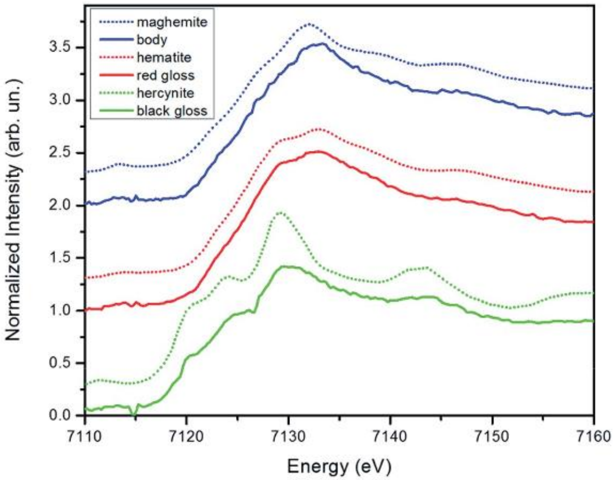
Supporting Information

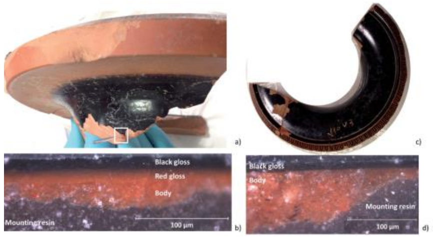
ABSTRACT: The decorated black- and red-figured Athenian vases (sixth and fifth century BC) and the plain black-glazed ware represent a milestone in our material culture due to their aesthetic and technological value; the Attic black glaze is of particular interest since it is a highly resistant potash−alumino−silicate glass, colored by magnetite nanocrystals (<200 nm). This study presents a new methodological approach for correlating the iron oxidation state in the black glaze layer with the manufacturing process by means of conventional and confocal X-ray absorption near edge spectroscopy (XANES). The enhanced surface sensitivity of confocal XANES is combined with conventional XANES resulting in higher counting rates to reliably evaluate the iron oxidation state ($Fe^{3+}/\Sigma Fe$) of the surface layer. A detailed description of the new evaluation procedure is presented. The three-stage firing process was retraced by correlating selected attic black-glazed (BG) specimens from different periods (Archaic, Classical, Hellenistic) with laboratory reproductions. The modern BG specimens serving as reference samples were produced by following the three-stage firing process (i.e., under oxidizing−reducing−oxidizing (ORO) conditions) at different top temperatures, using clay suspensions of different particle size produced with treatment of raw illitic clays from Attica.











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Evidence for an unorthodox firing sequence employed by the Berlin Painter: deciphering ancient ceramic firing conditions through high-resolution material characterization and replication

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Chemical, electronic, and structural information **(2.4 - 68 keV)**

CLÆSS beamline performance:

- Beam size up to 100 x 200 μm^2
- Continuous scan (5-10 min scan)
- XAS in transmission and fluorescence detection mode
- XES – *from 6.4 to 9.3 keV (Kβ and Kα of most of the transition metal)*
- Stable beam-position and beam-size (200-500 μm) in the full energy range
- Temperature control from 80 K to 800 K; or from 4 K to 300 K
- In-situ cell for solid-gas reactions (80 K – 700 K)