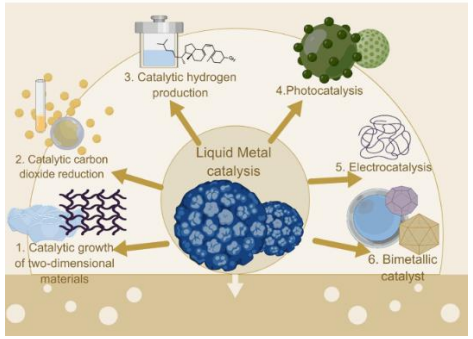
Elettra Sincrotrone Trieste

Case Studies of XAS Applications

Min Li

22/10/2024

Batterie Materials



Catalysts

Cultural Heritage

Environment Science

DOI: https://doi.org/10.1007/978-981-19-2797-3_48-1

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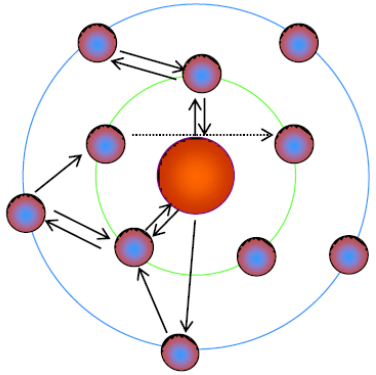
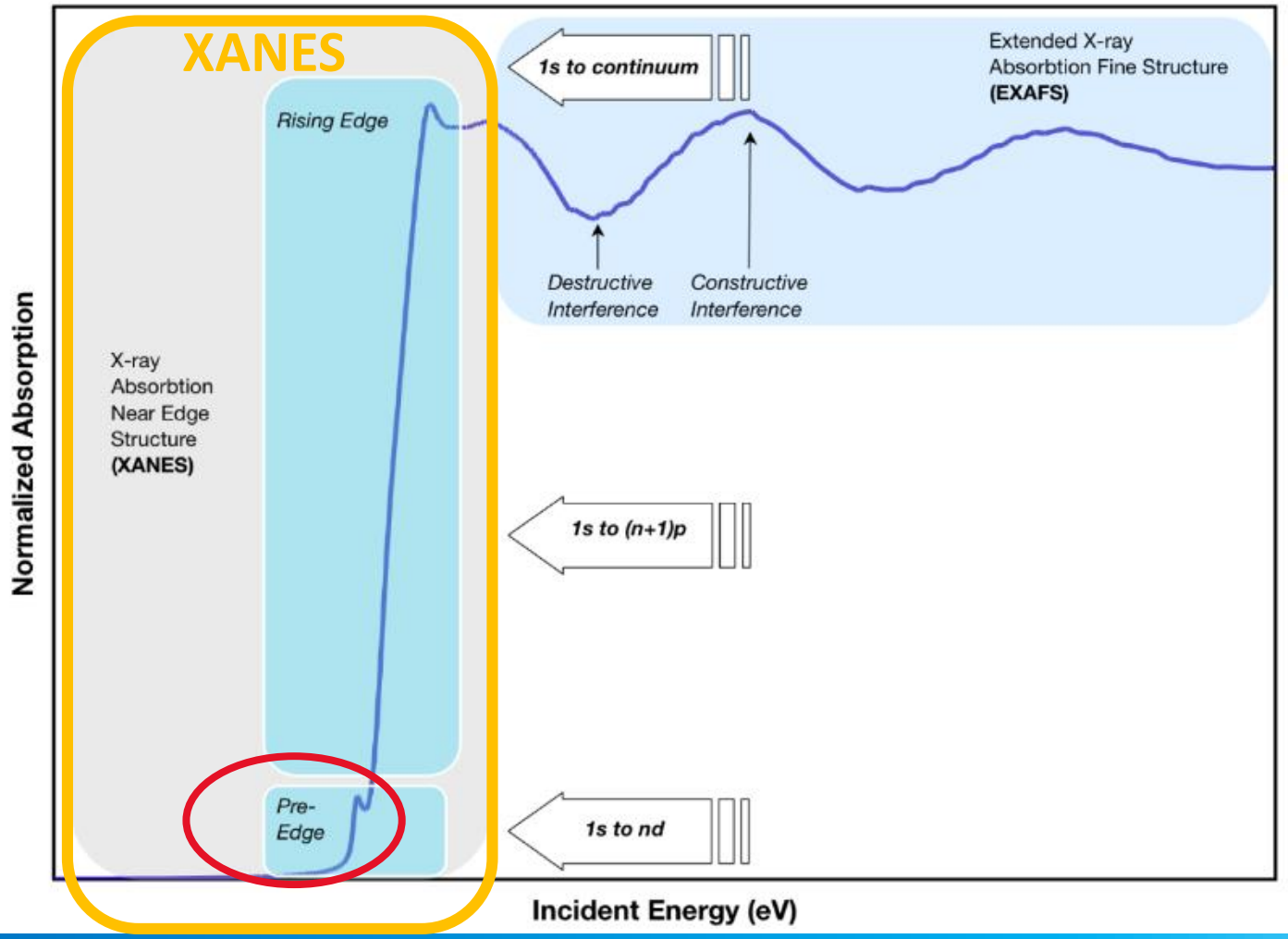
XAS Data Information (XAS= XANES+ EXAFS)

-XANES X-ray Absorption Near Edge Structure

-EXAFS Extended X-ray Absorption Fine Structure





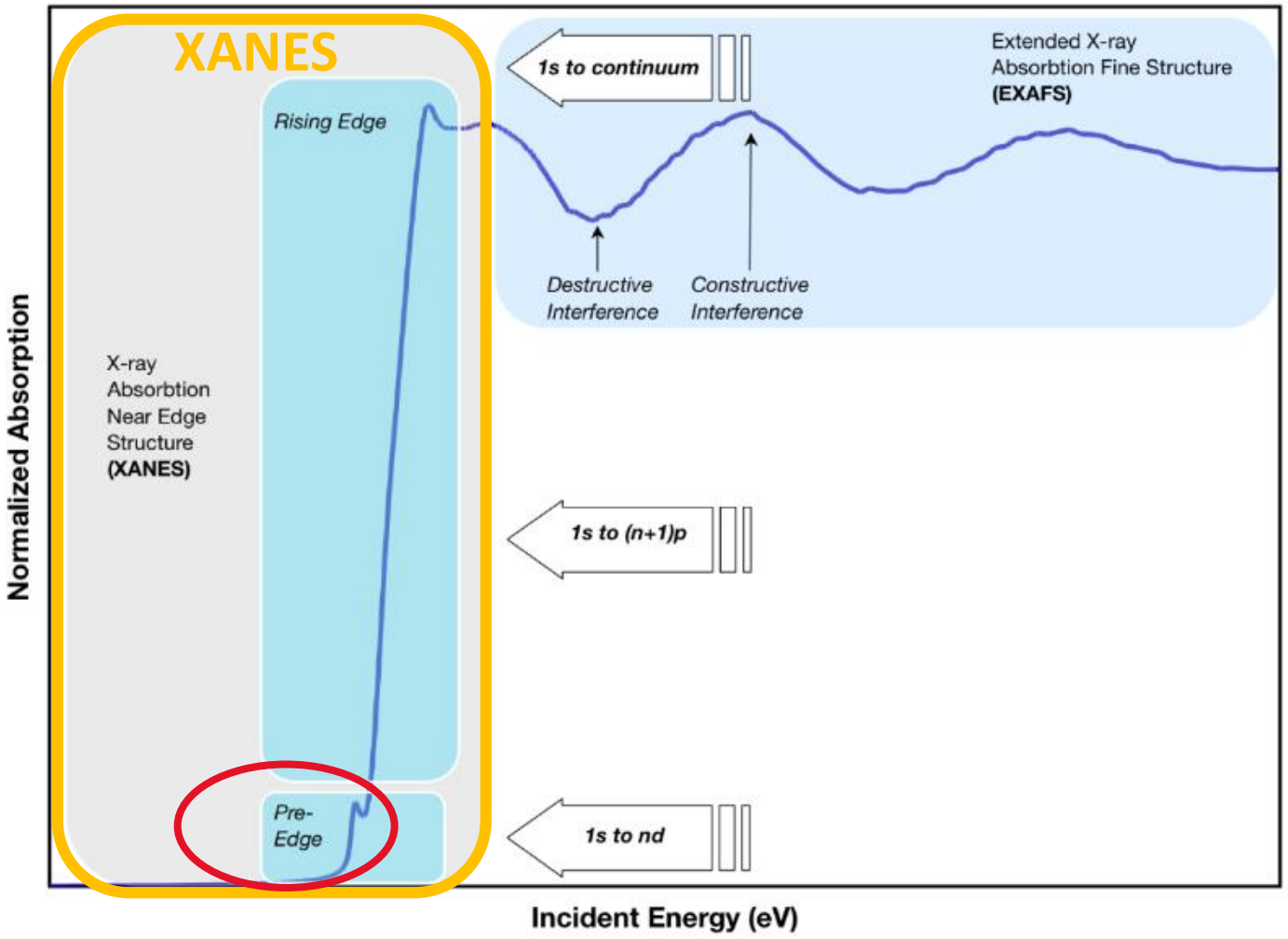
- Covalency
- Electronic Structure
- Site Symmetry
- Oxidation State

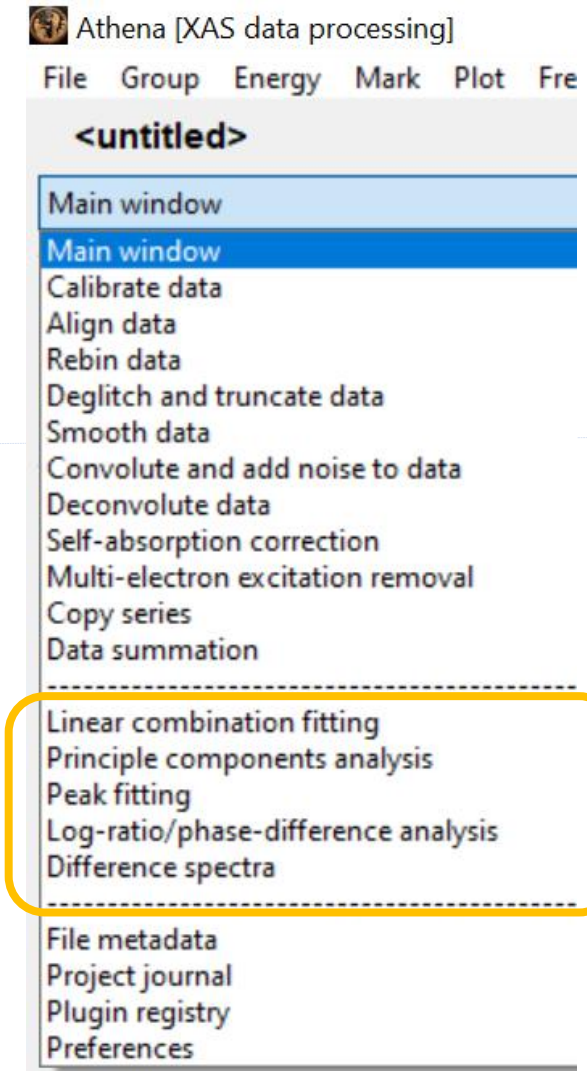
https://en.wikipedia.org/wiki/X-ray_absorption_spectroscopy

XAS Data Information (XAS= XANES+ EXAFS)

-XANES X-ray Absorption Near Edge Structure

-EXAFS Extended X-ray Absorption Fine Structure





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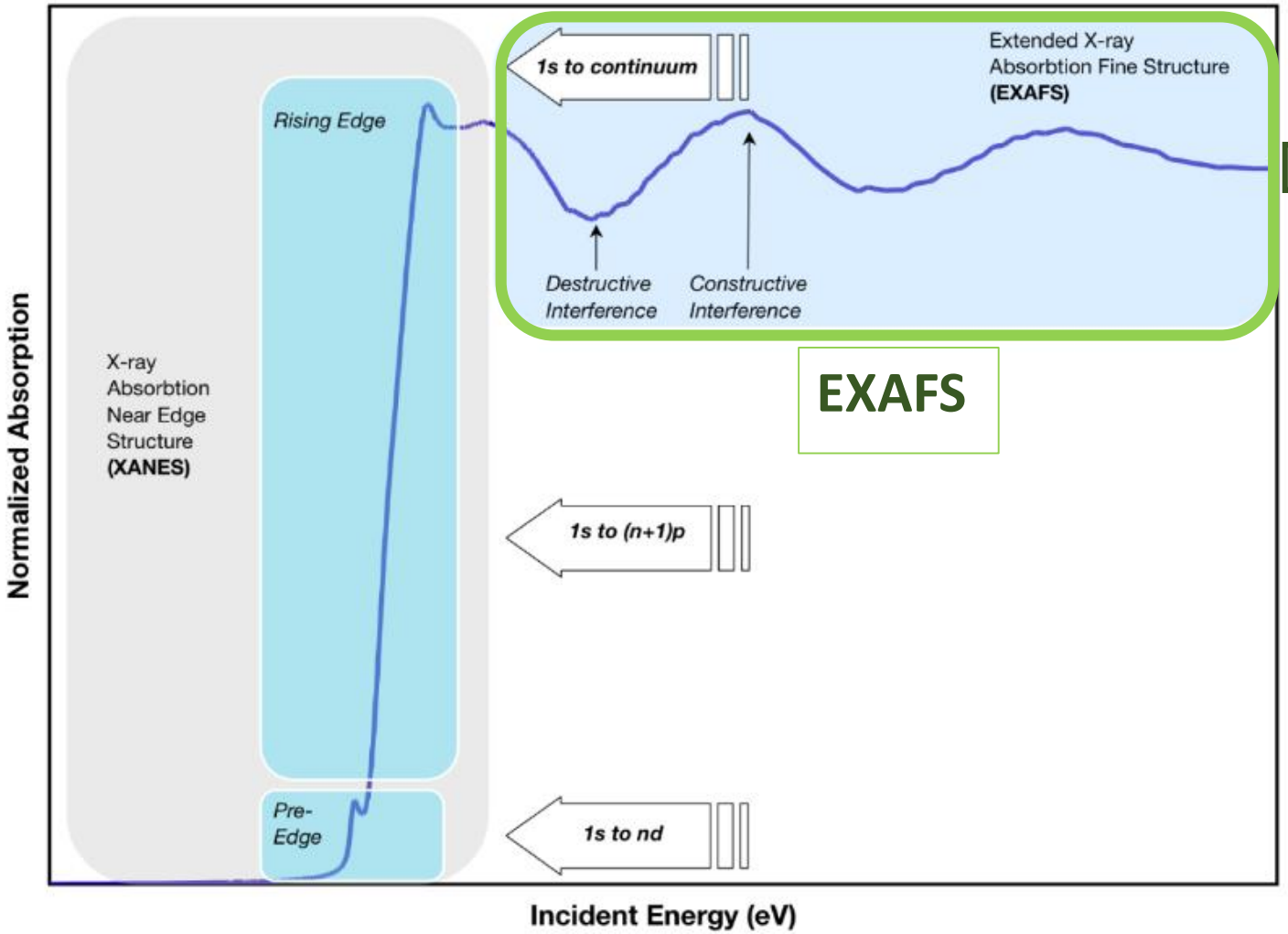
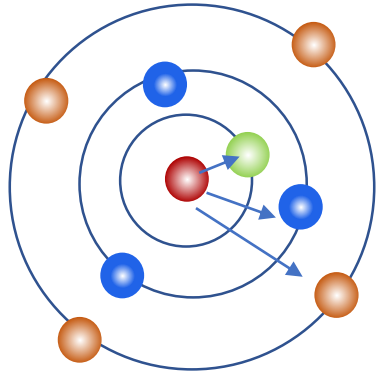
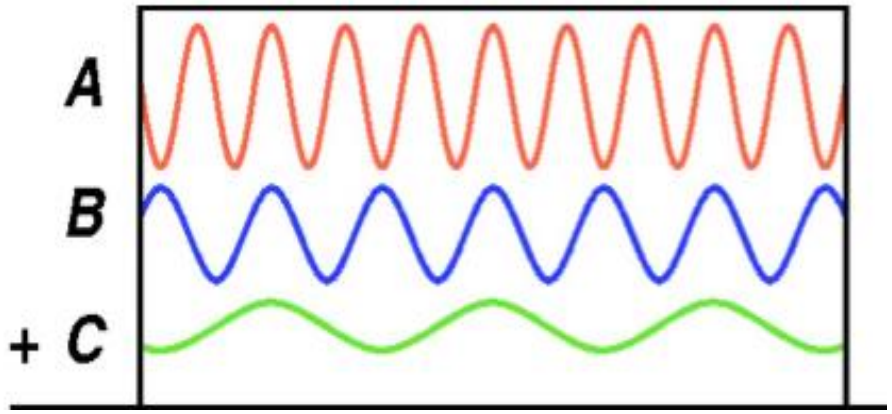
EXAFS



FT





EXAFS=A+B+C

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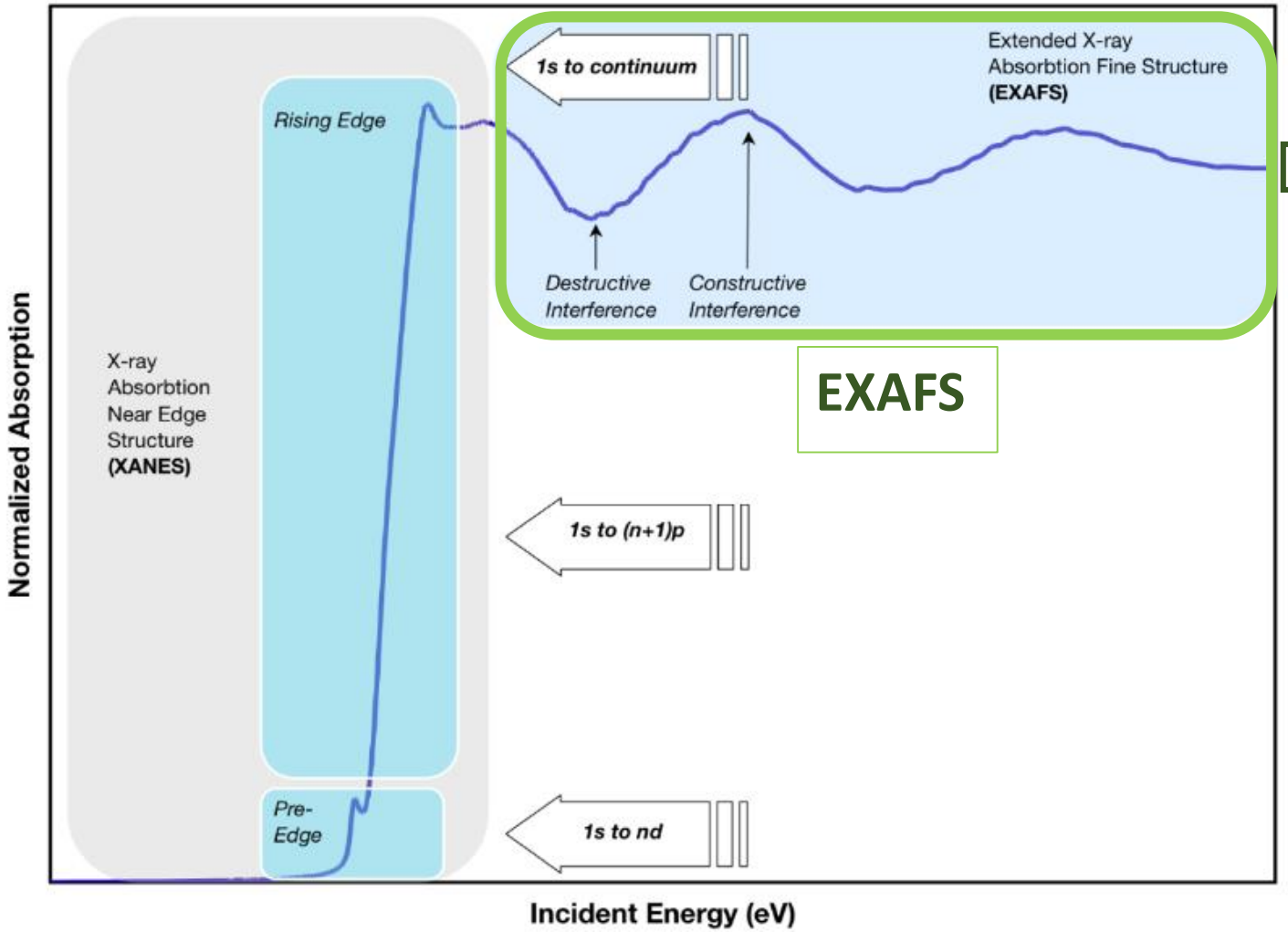
EXAFS



FT

- **Types of Ligands**
- **Bond Distances**
- **Coordination Numbers**

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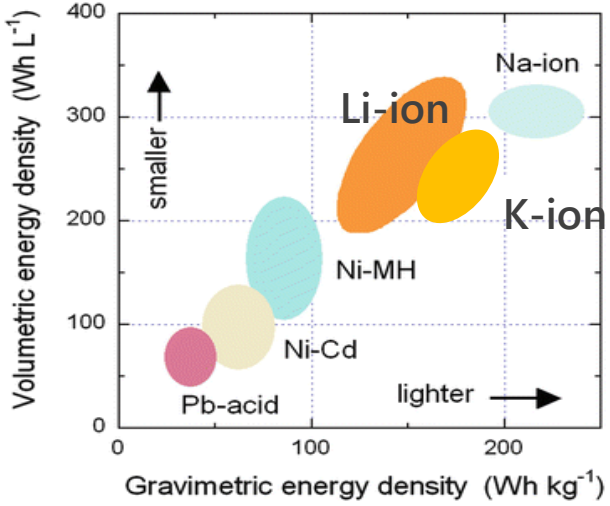
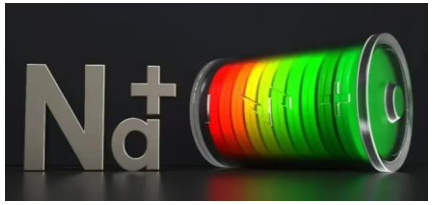
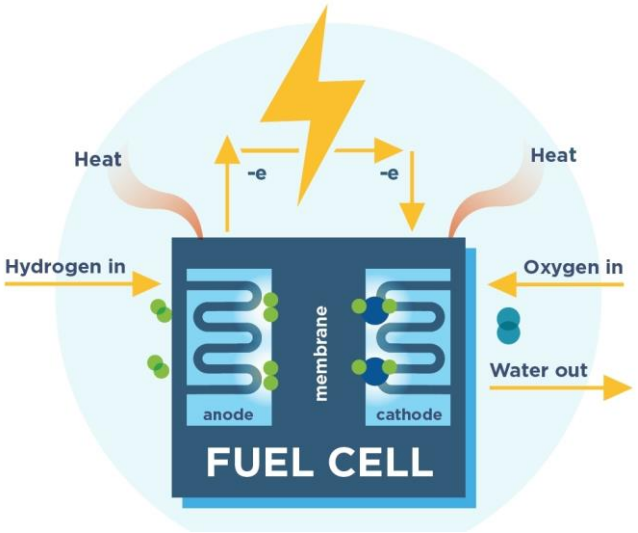
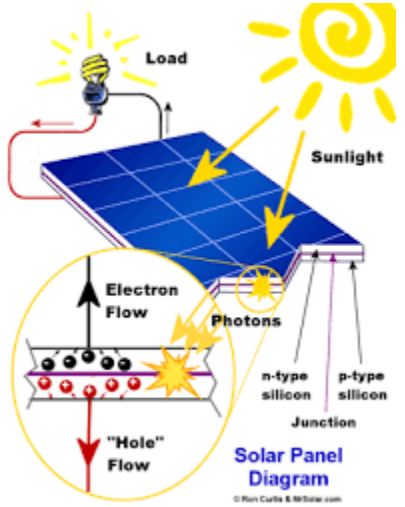
Application 1:

Battery Materials_Opernado/Ex-situ test









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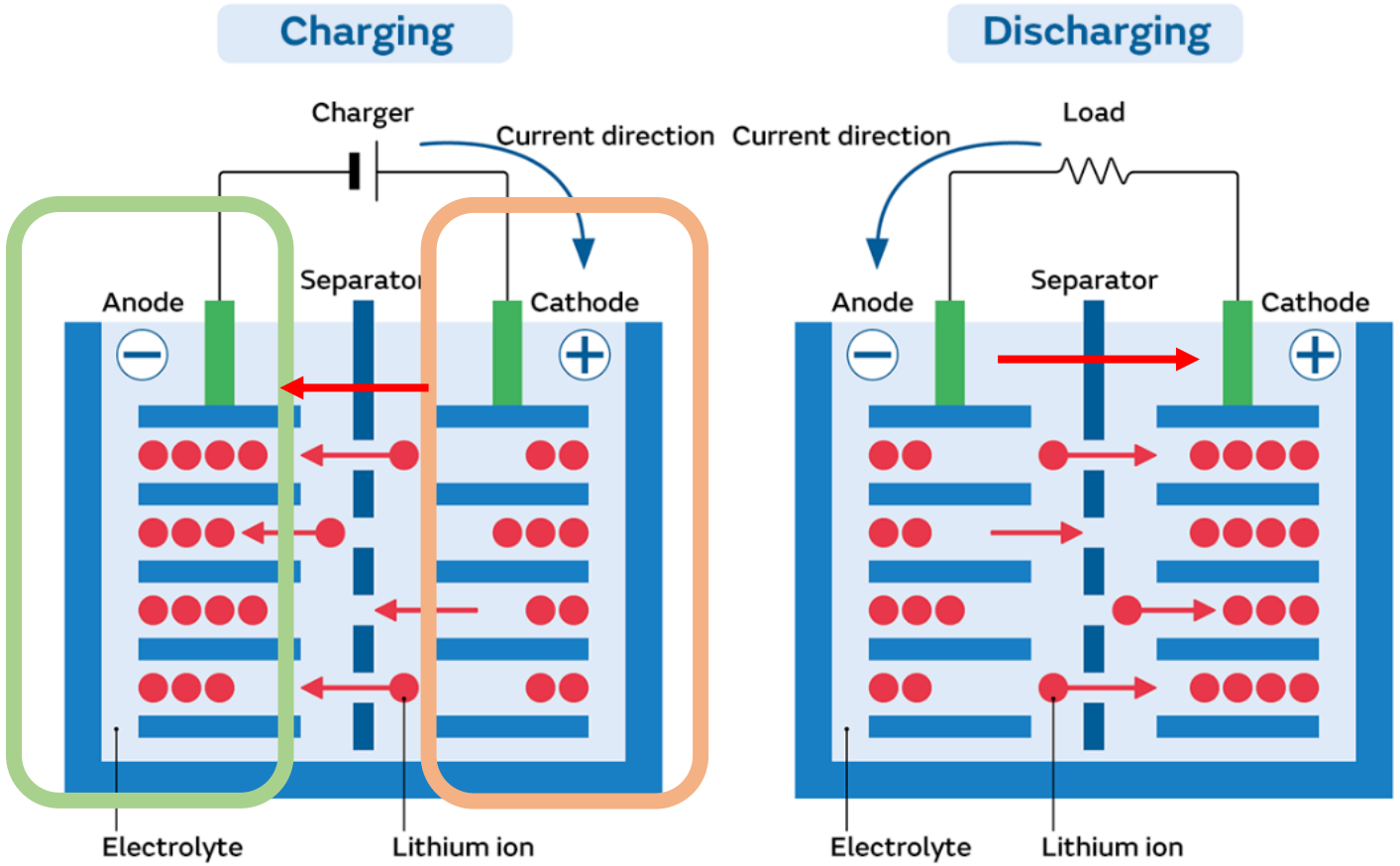
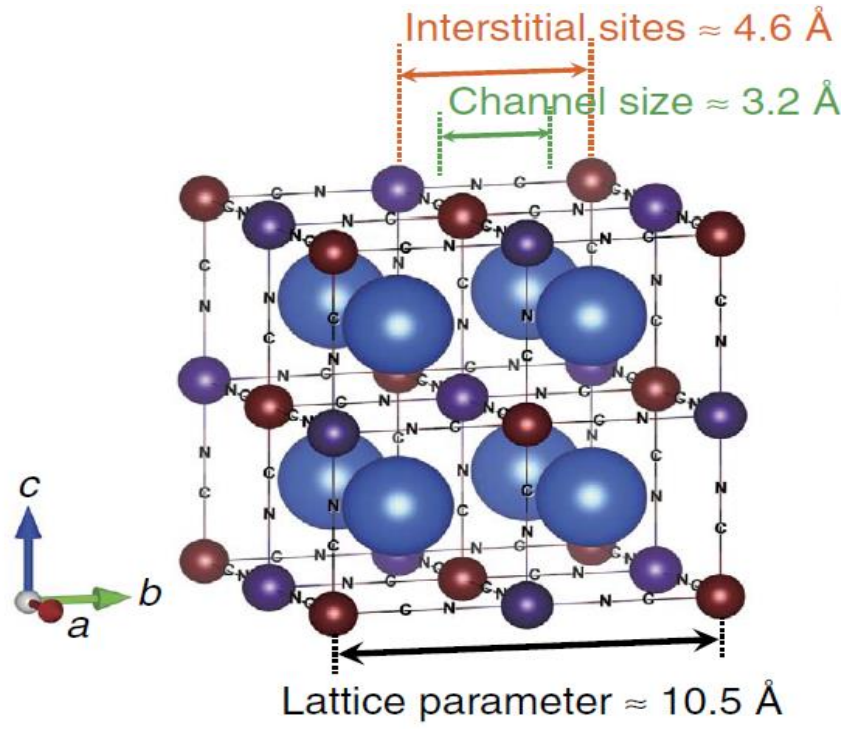
Schematic of the Working Mechanism of a Lithium-ion Battery:





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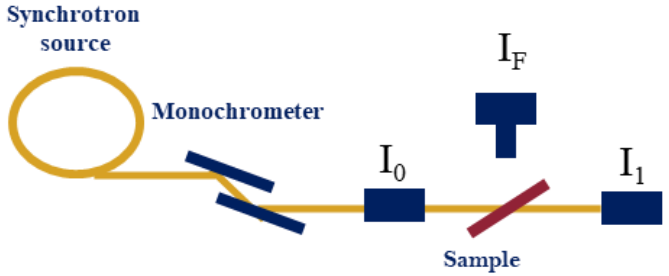
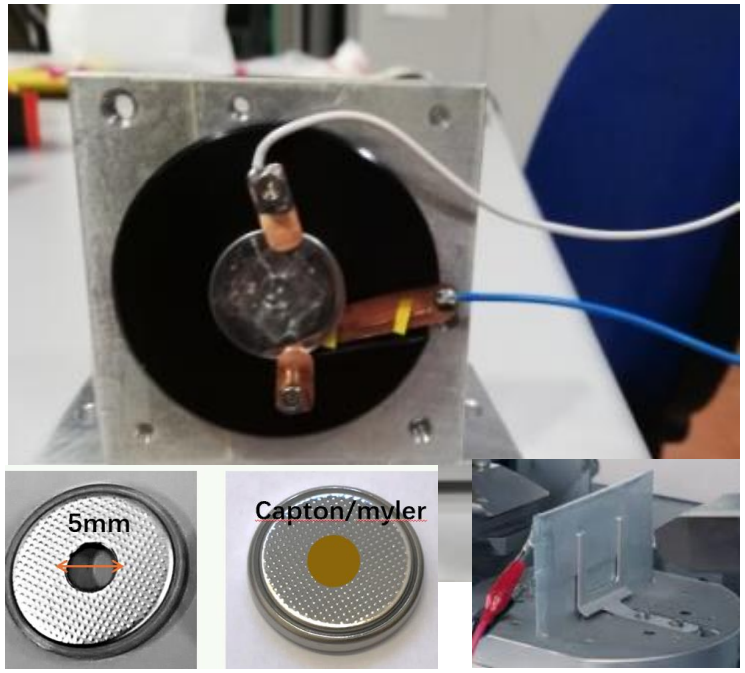
Trieste

The Operando Battery Test Set-up



Battery



Transition mode

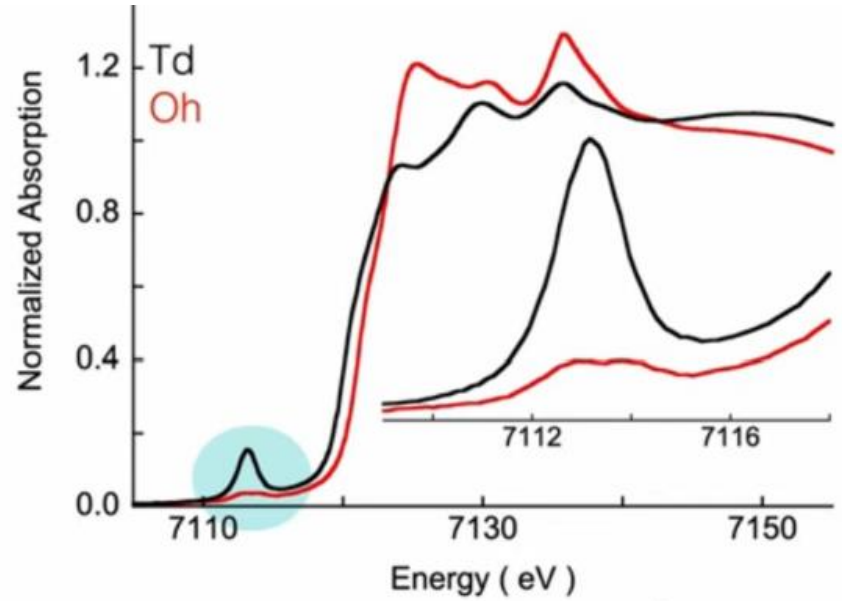
Fluorescence mode

❑ Identification of Metal Electroactivity from the Pre-edge

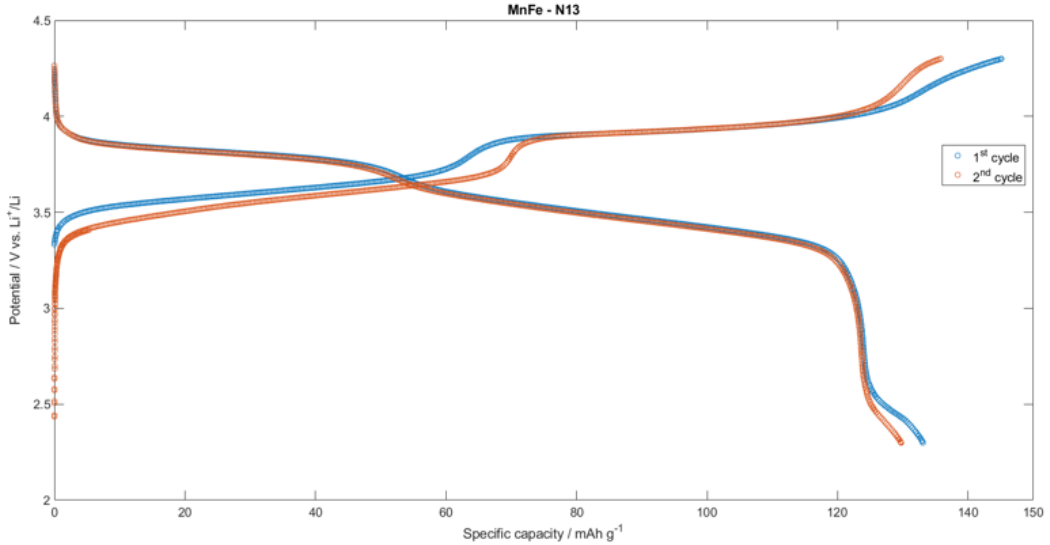
THE JOURNAL OF PHYSICAL CHEMISTRY C
Article
Cite This: J. Phys. Chem. C 2018, 122, 15868−15877
pubs.acs.org/JPCC

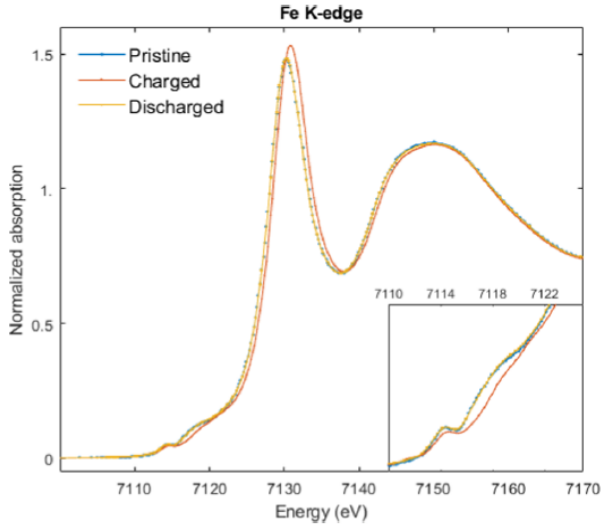
Copper Electroactivity in Prussian Blue-Based Cathode Disclosed by Operando XAS

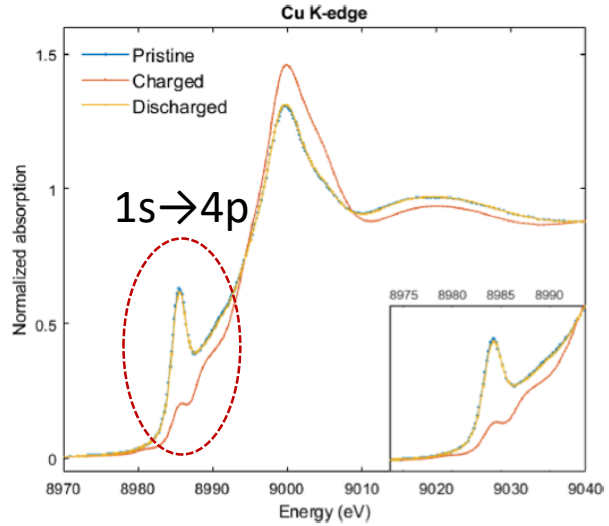
Angelo Mullaliu,[†] Giuliana Aquilanti,[‡] Paolo Conti,[§] Jasper R. Plaisier,[‡] Marcus Fehse,[∥] Lorenzo Stievano,[*,⊥,#] and Marco Giorgetti[*,†]



-Cu-NC-Fe-





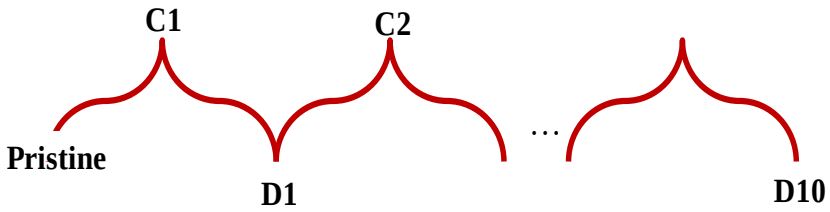


- The evolution of the pre-edge peak confirms the electroactivity of Cu sites.

the 1s−4p transition indicates mainly Cu^{I}

❑ Linear Combination Fitting (LCF) of XANES

Ex-situ electrodes:

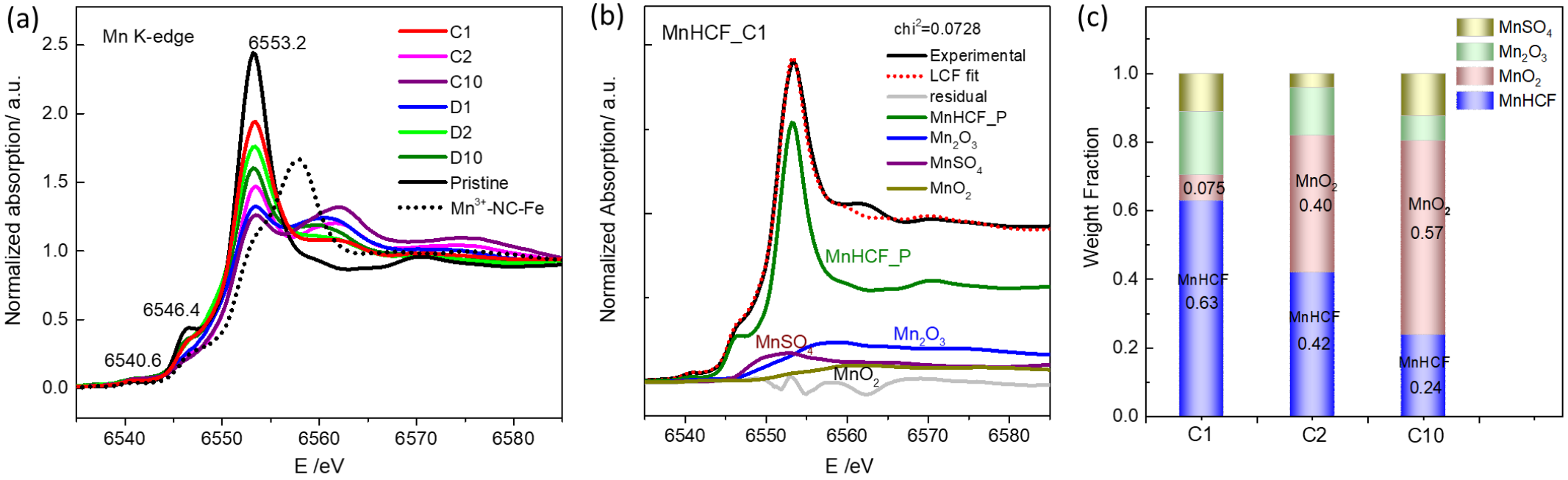


*C1: first charge; D1: first discharge

Aquesous Zn-ion Battery

-Mn-NC-Fe-

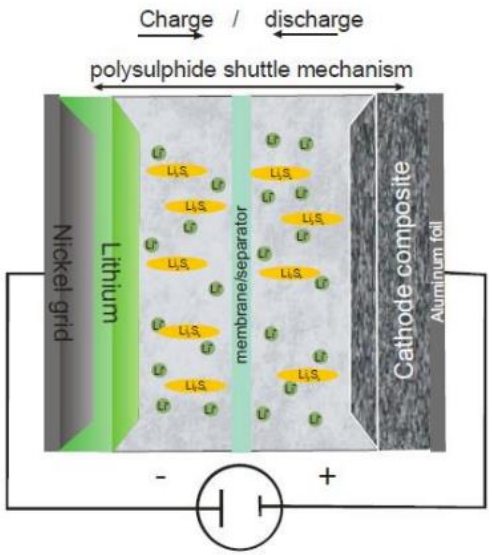
(Mn^{2+} , Mn^{3+} , Mn^{4+} , Mn^{6+} , Mn^{7+})



- To interpret the kinetics (intermediate spectrum) of series of spectra measured during a reduction/oxidation reaction.
- To identify the species and quantities of standards in a heterogeneous sample.

❑ Linear Combination Fitting (LCF) of XANES

Li-S battery



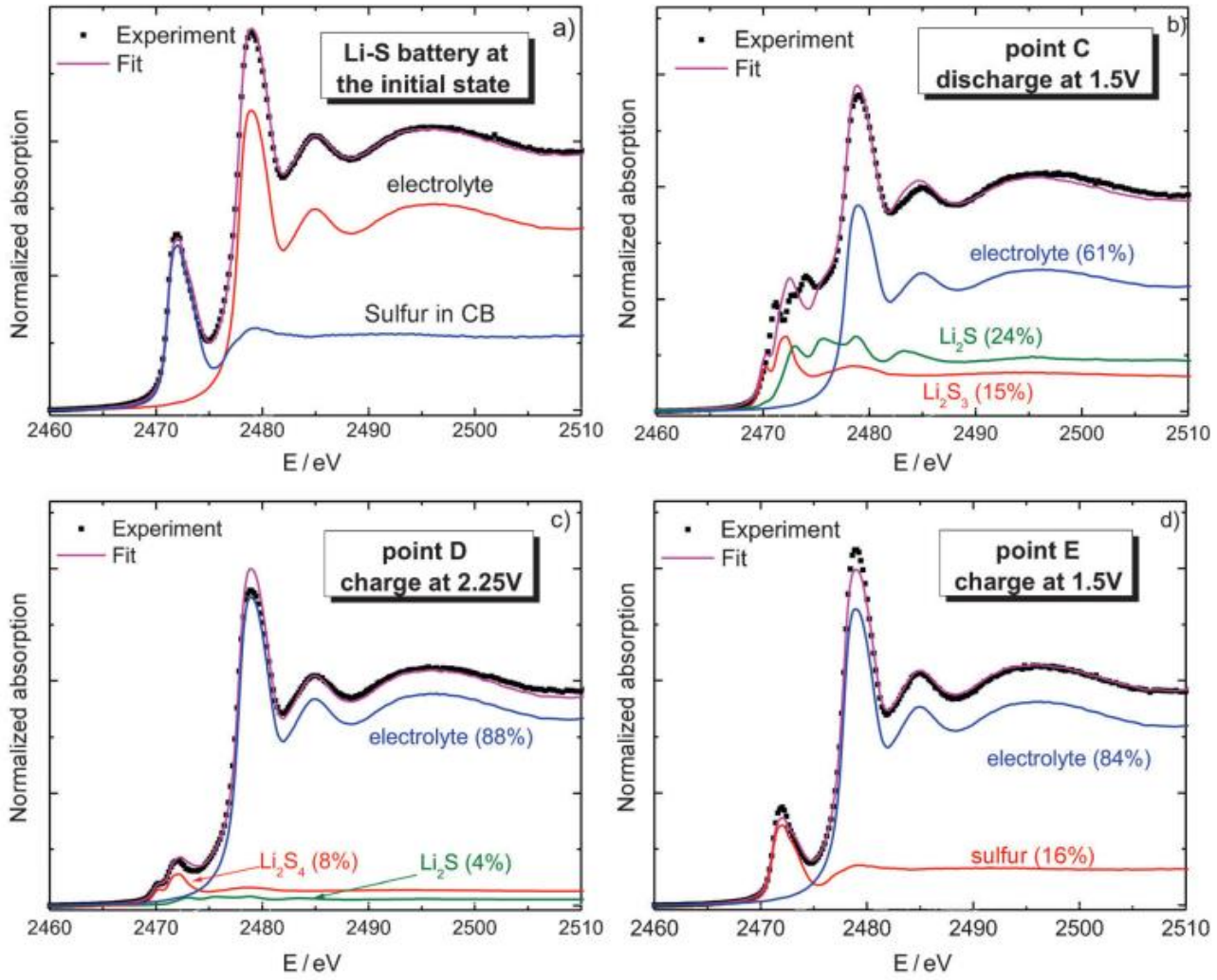
$$S_8 + Li^+ + e^- \rightarrow Li_2S_x$$

(2.4 – 2.1 V)

$$Li_2S_x + Li^+ + e^- \rightarrow Li_2S_2 \text{ and/or } Li_2S$$

(2.1 – 1.5 V)

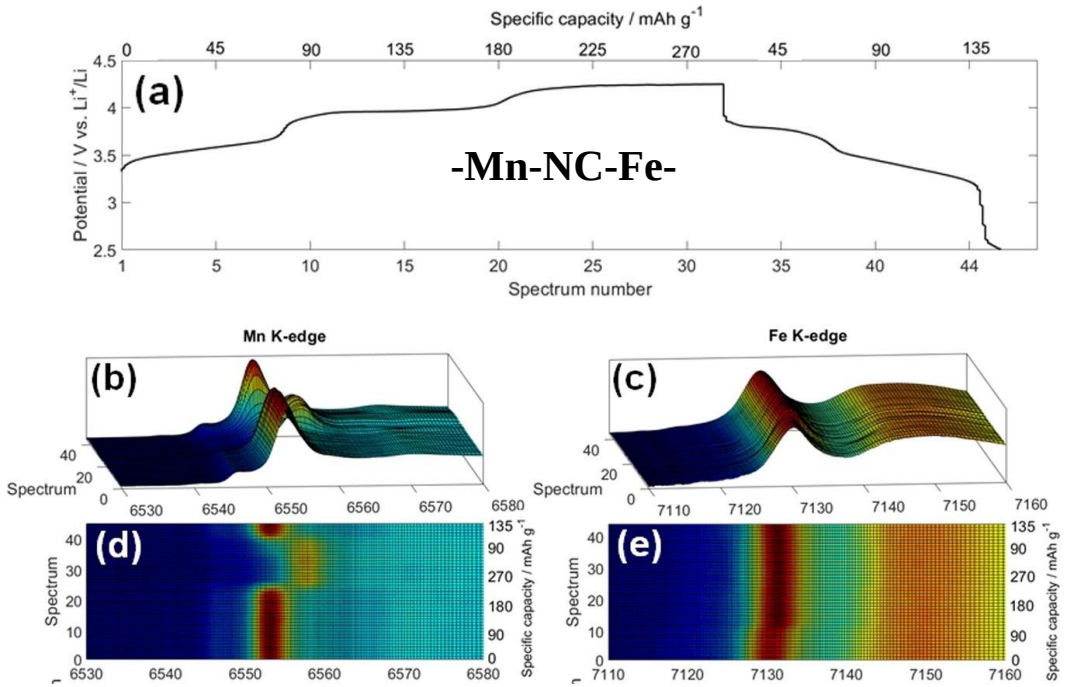
The reactions include solid-liquid-solid transformation, causing great complexity

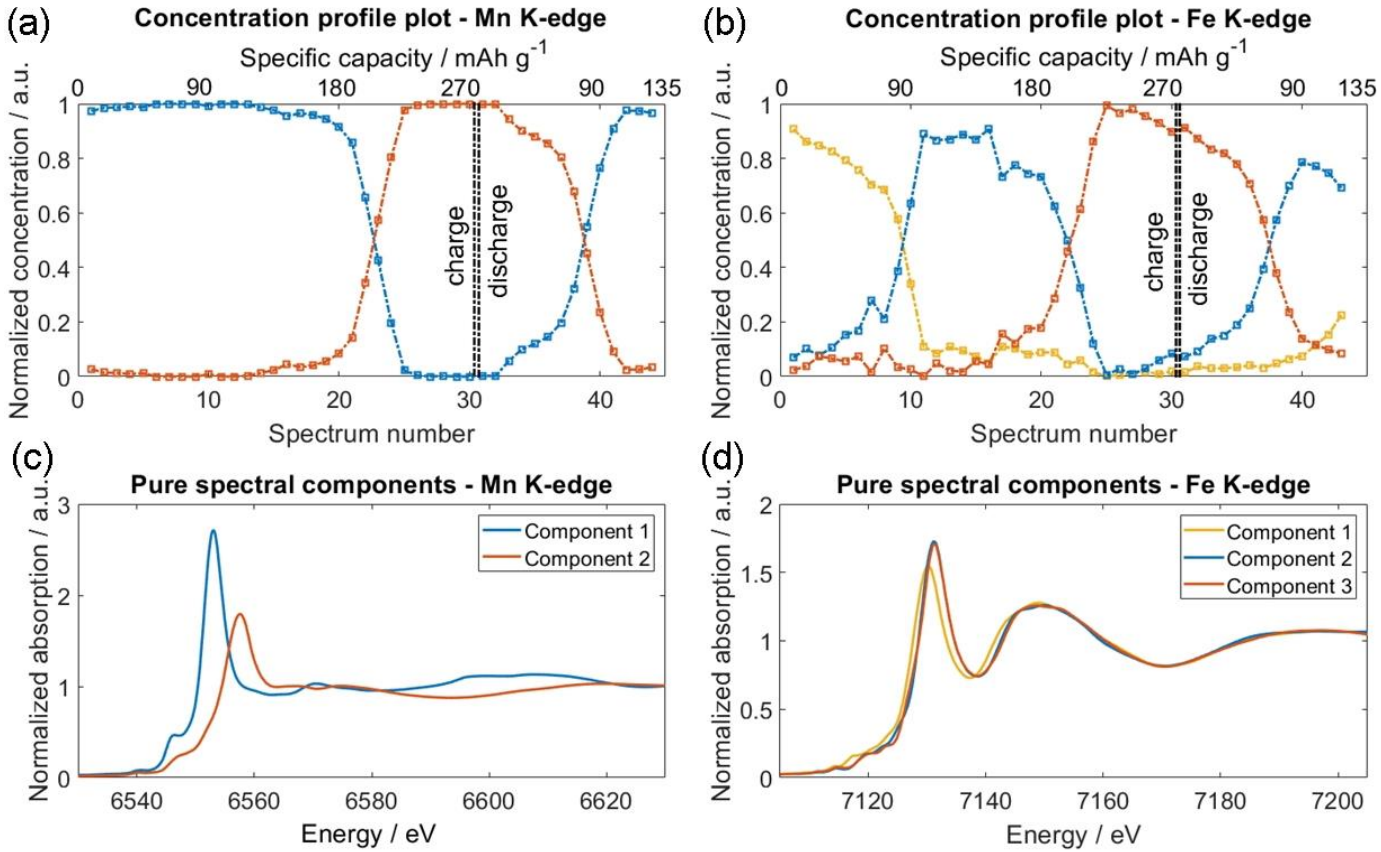


➢ To determine the relative amount of the different sulfur species by LCF

❑ Chemometric Analysis of XANES Spectra

- **Principal component analysis (PCA)**
- **Multivariate Curve Resolution-Alternating Least Square (MCR-ALS)**





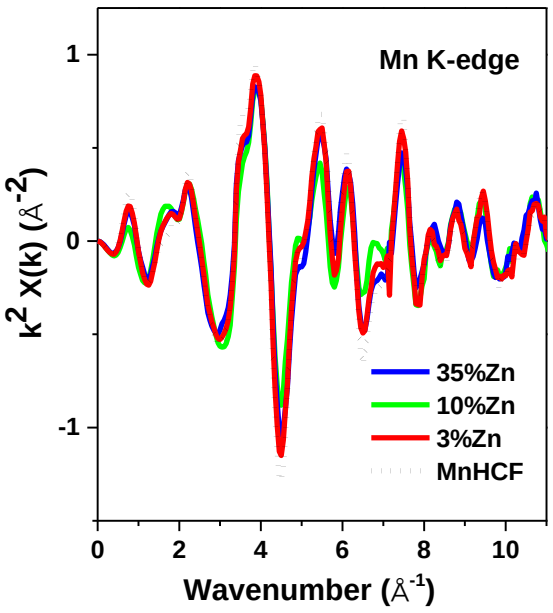
➢ Analyze the components change during Charge/discharge process.

❑ Quantifying Jahn-Teller Distortion by EXAFS

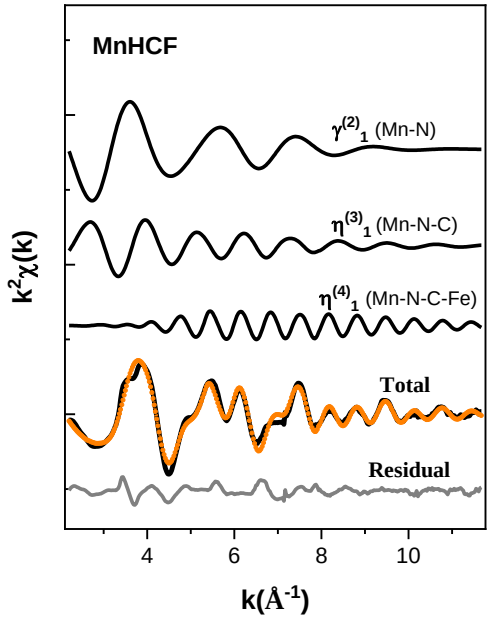
FULL PAPER
Reversible Jahn-Teller Effect
small methods
www.small-methods.com

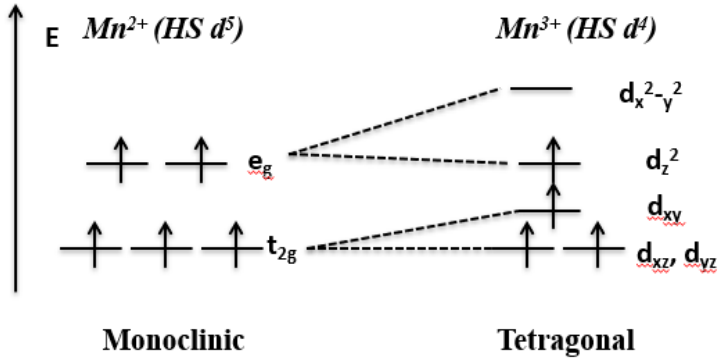
Highlighting the Reversible Manganese Electroactivity in Na-Rich Manganese Hexacyanoferrate Material for Li- and Na-Ion Storage

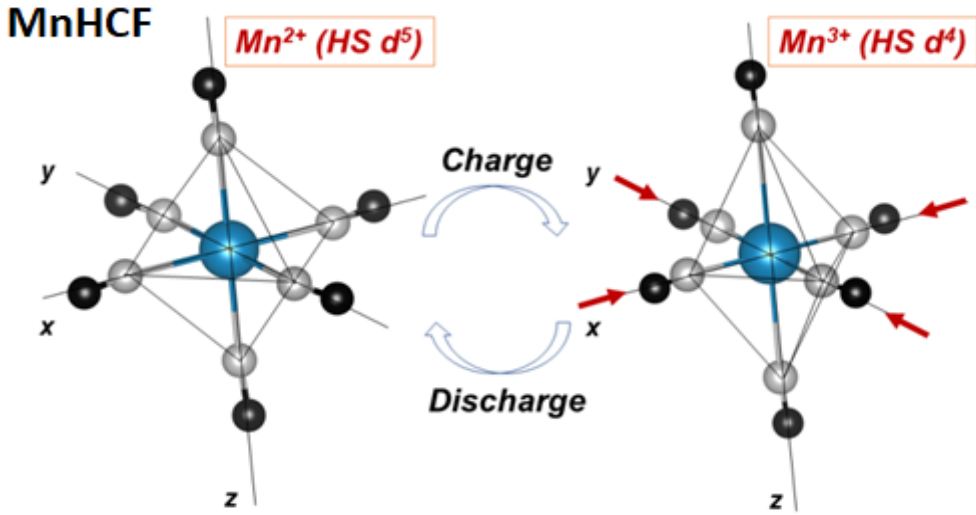
Angelo Mullaliu, Jakob Asenbauer, Giuliana Aquilanti, Stefano Passerini, and Marco Giorgetti**



-Mn-NC-Fe-







Equatorial Mn-N distances shrunk by 10% (2.18 Å → 1.96 Å)

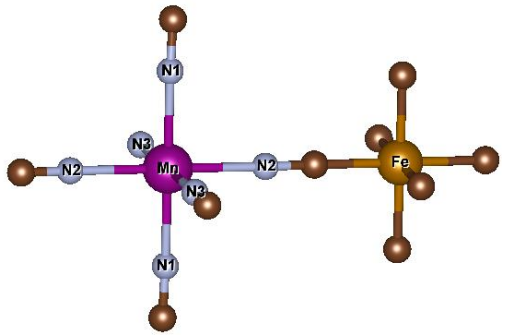
❑ Confirm the Coordination States Change by EXAFS Fitting

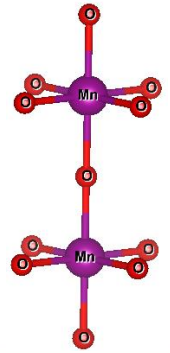
RESEARCH ARTICLE

NANO · MICRO small
www.small-journal.com

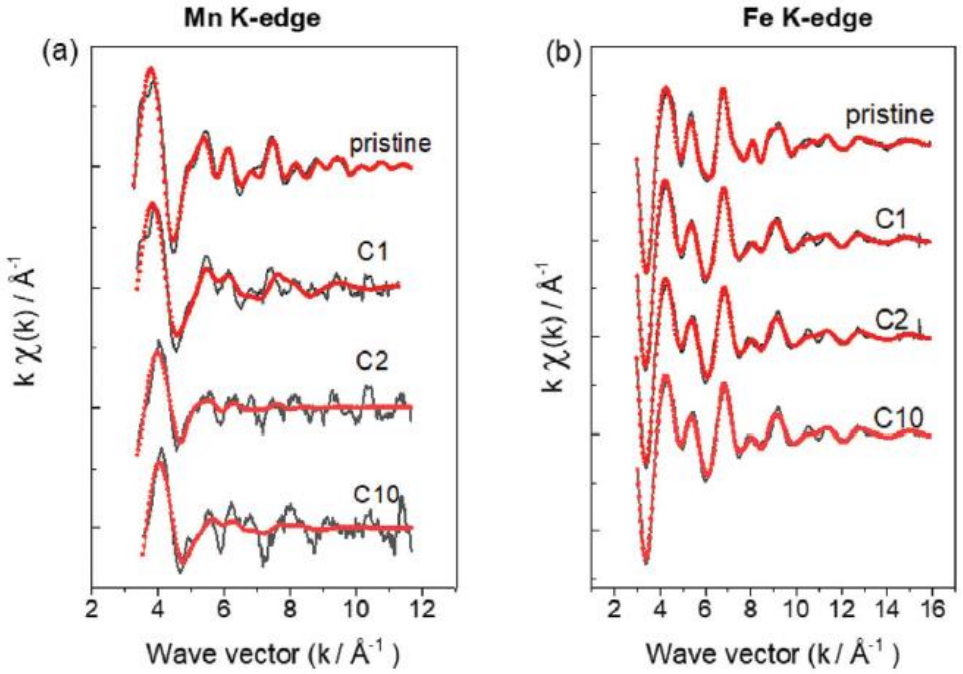
Structural Evolution of Manganese Prussian Blue Analogue in Aqueous $ZnSO_4$ Electrolyte

*Min Li, Mariam Maisuradze, Angelo Mullaliu, Ilaria Carlomagno, Giuliana Aquilanti, Jasper Rikkert Plaisier, and Marco Giorgetti**

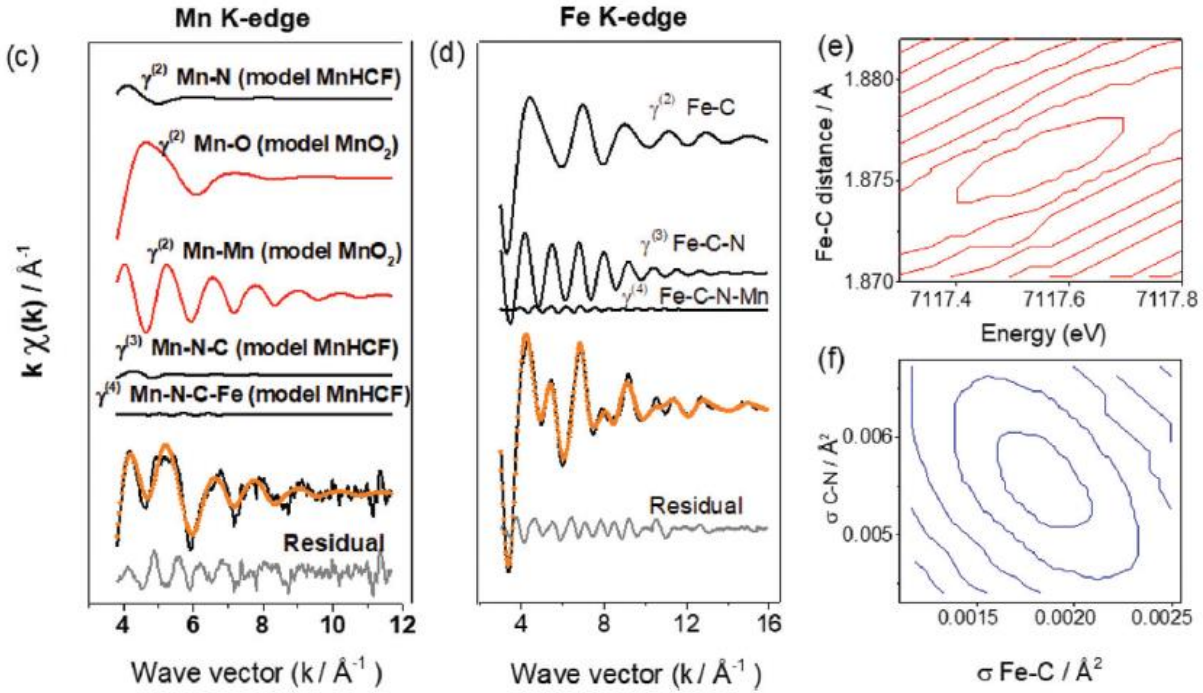




One-model EXAFS fitting

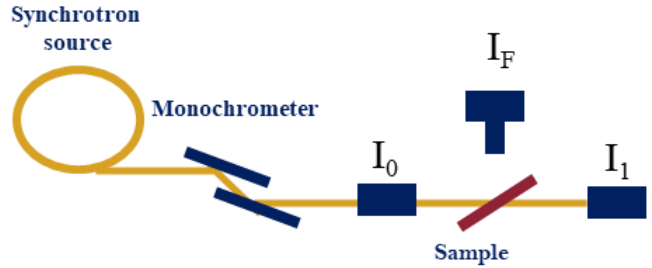


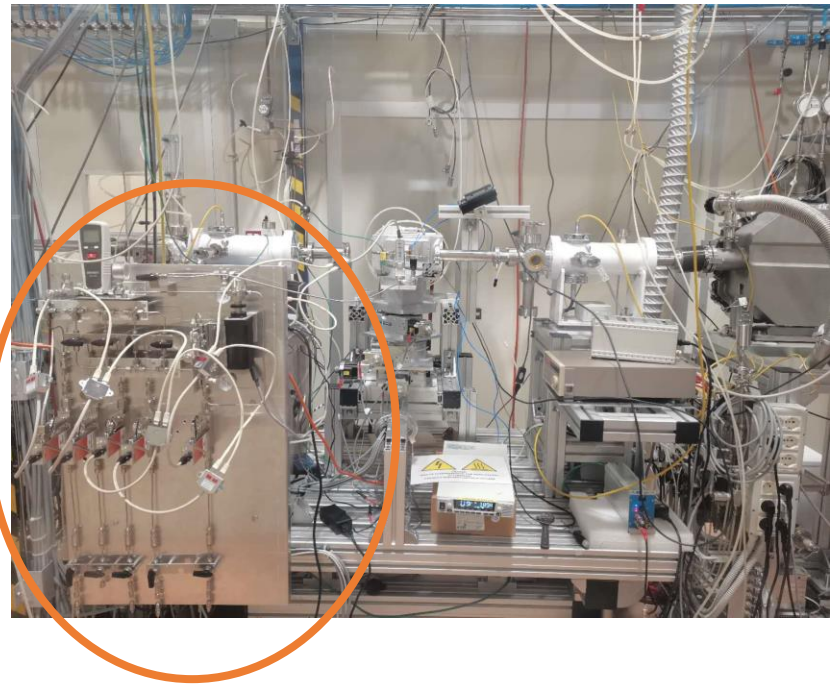
C10- Two models EXAFS fitting

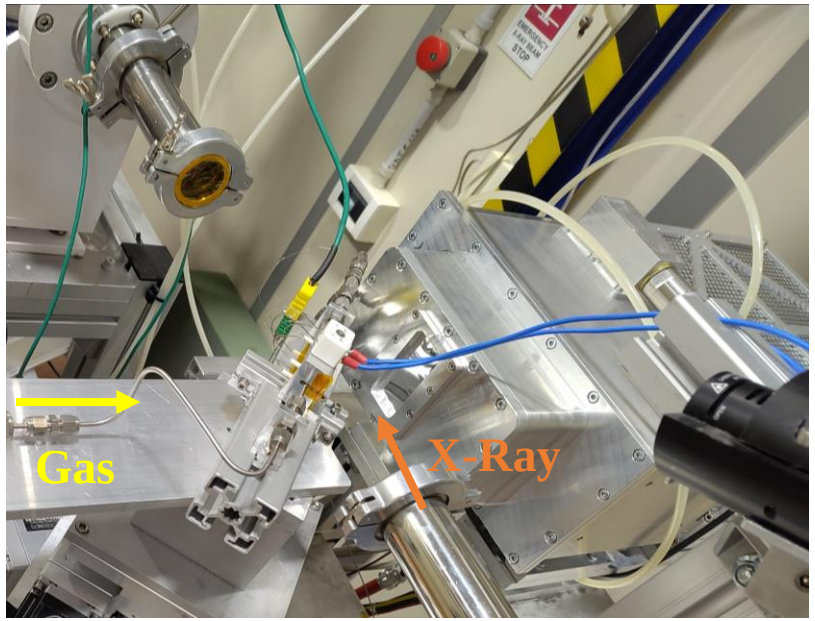


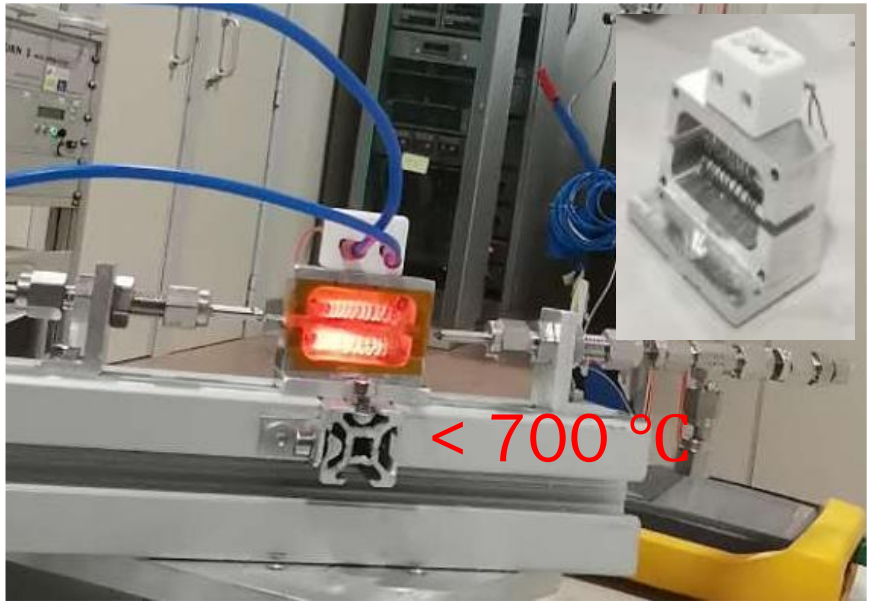
Application 2: Catalyst Materials_Operando or Ex-situ Tests

The Operando Capillary Gas-System Set-up









- A series of Catalytic/Electrocatalytic reactions, as well as in situ Temperature Scan experiments can be conducted.

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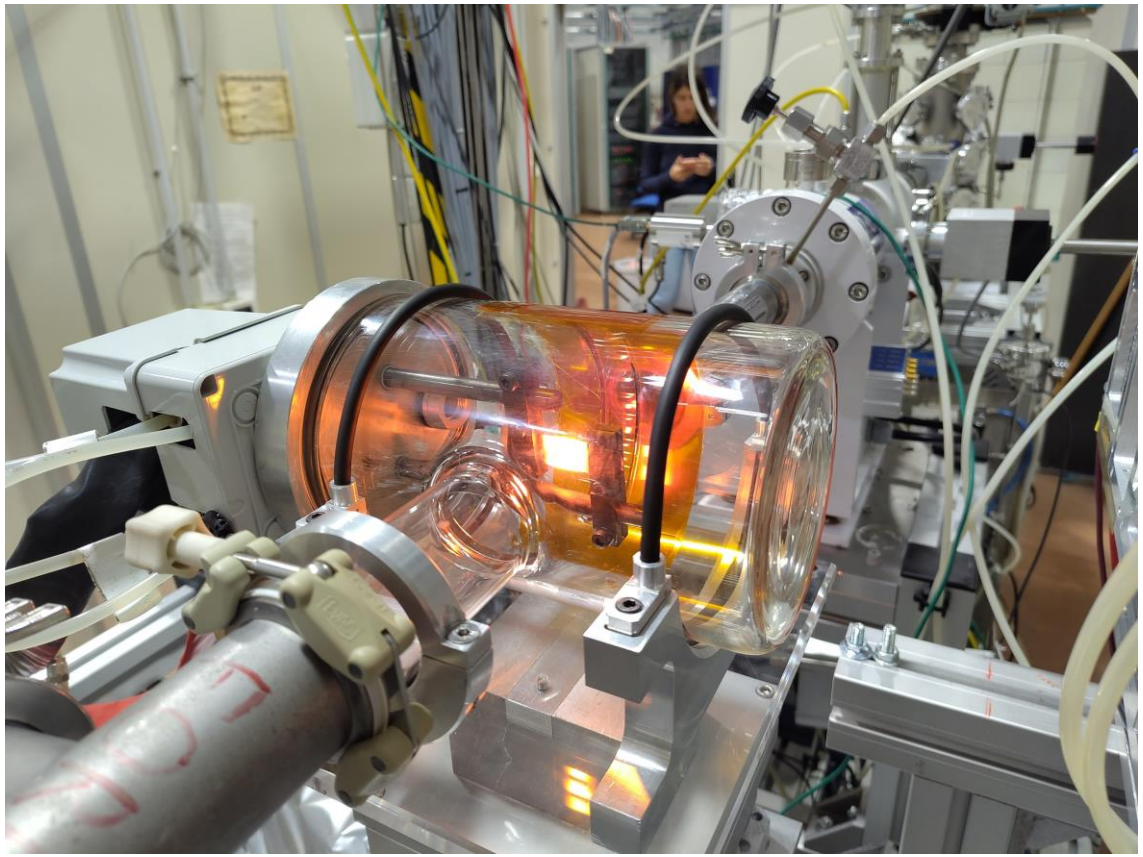
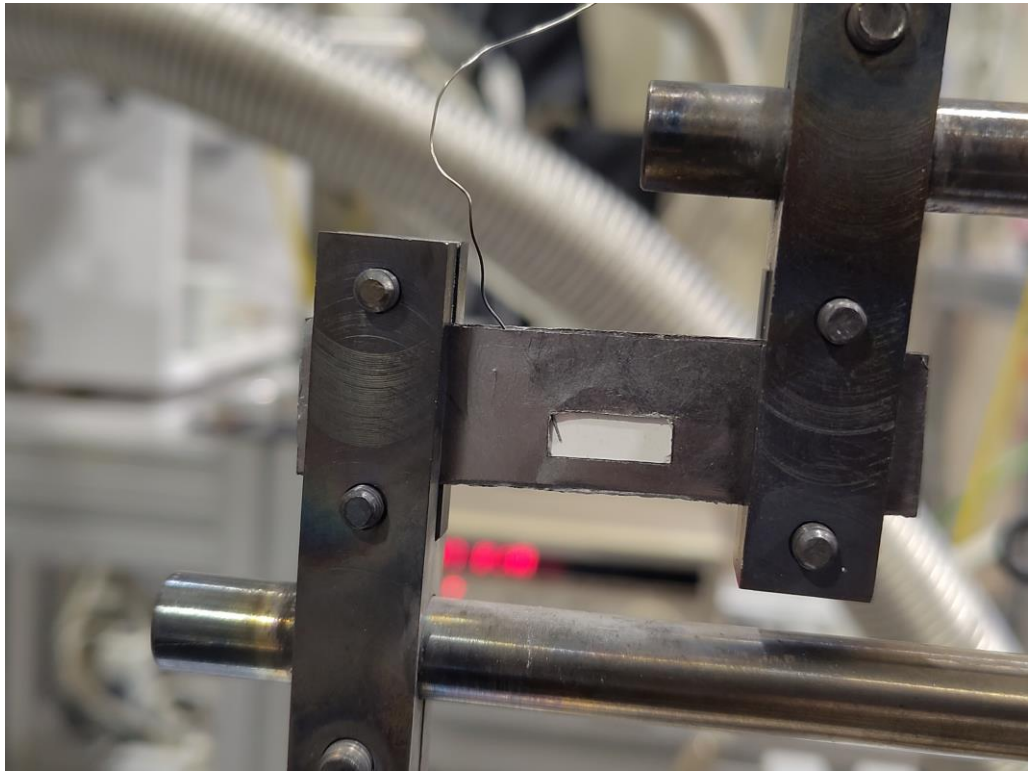
High Temperature Furnace under Vacuum

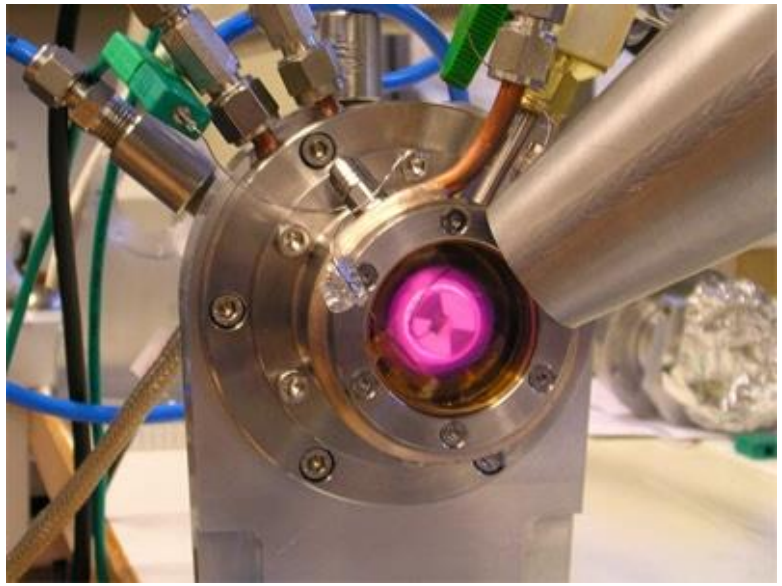
Temperature : from RT to 2500 C, vacuum below 10^{-5} mbar





Graphite resistive foil

Cells for in situ measurements



Sample environment pool@ESRF (Grenoble, France)

Maximum temperature 700°C

Max pressure 20 bar

Working in controlled atmosphere

Sample in self supported pellet

Fluo and transmission configuration

Coupled with Mass Spectroscopy

Maximum temperature 850°C

Working in controlled atmosphere

Sample in pellet form

Fluorescence configuration only

Coupled with Mass Spectrometer

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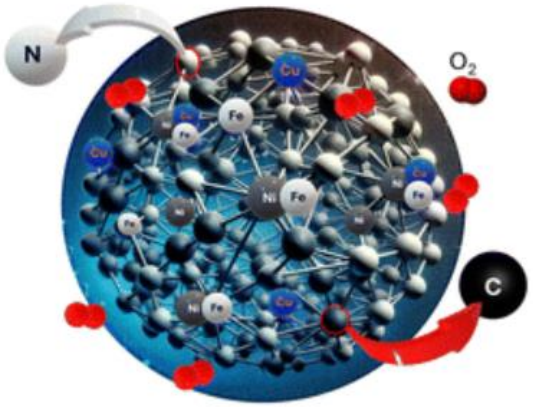
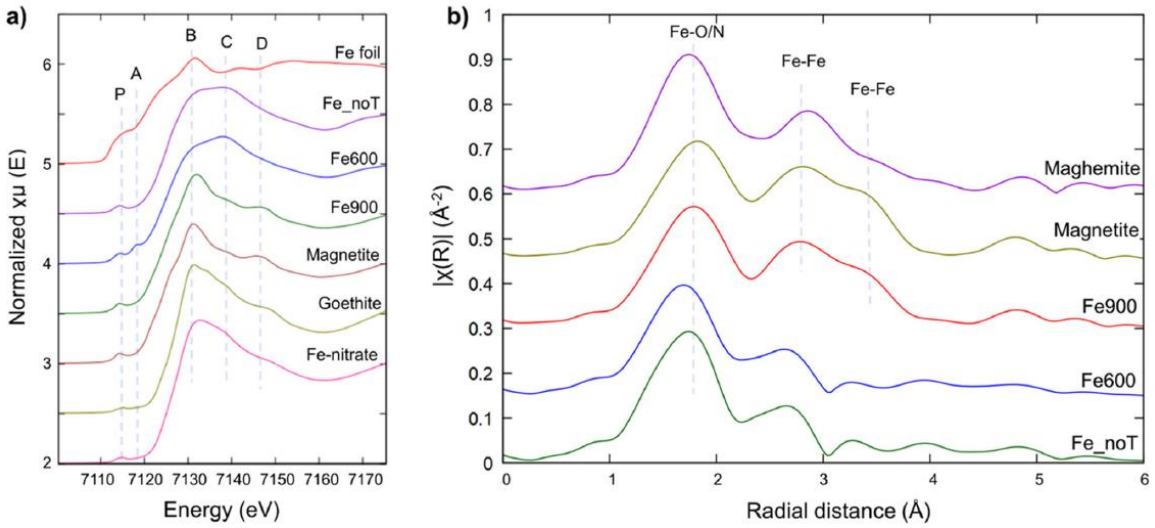
❑ Oxygen Reduction Reaction

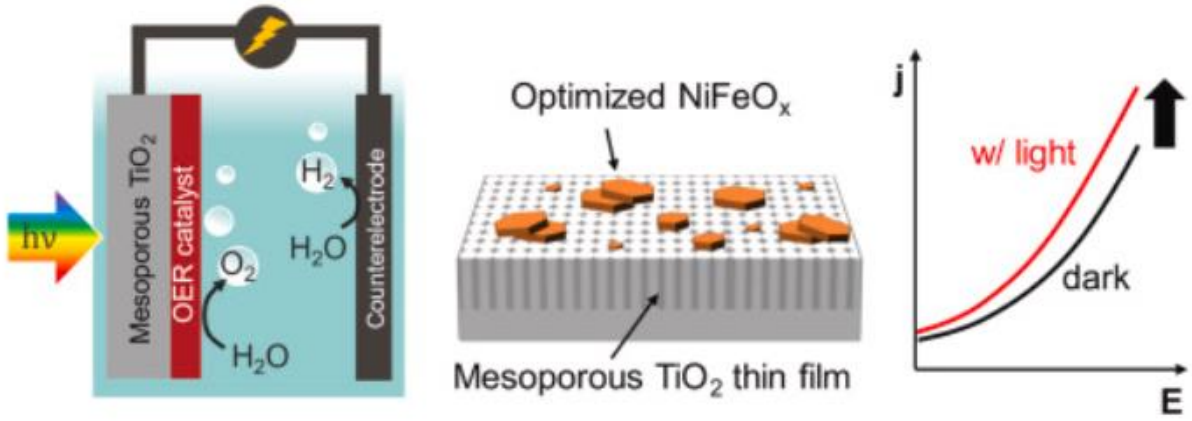


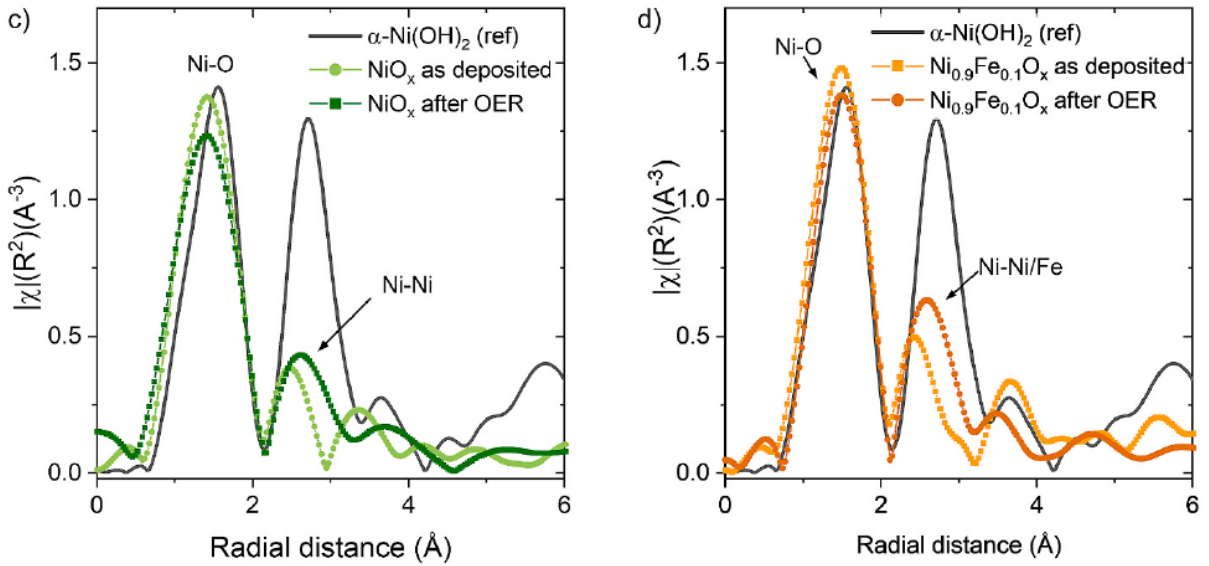
Mono-, bi- and tri-metallic Fe-based platinum group electrocatalysts



➢ Structure change

❑ Photocatalytic Reaction





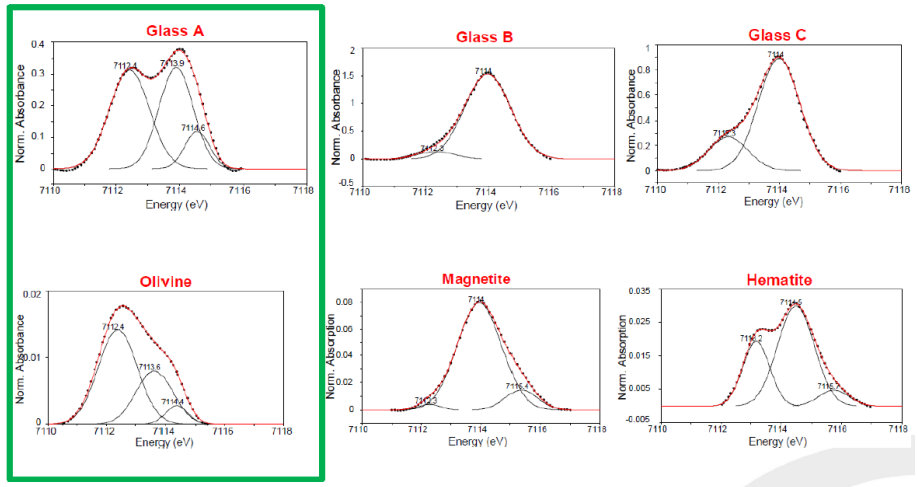
➢ phase transitions

Application 3: Cultural Heritage

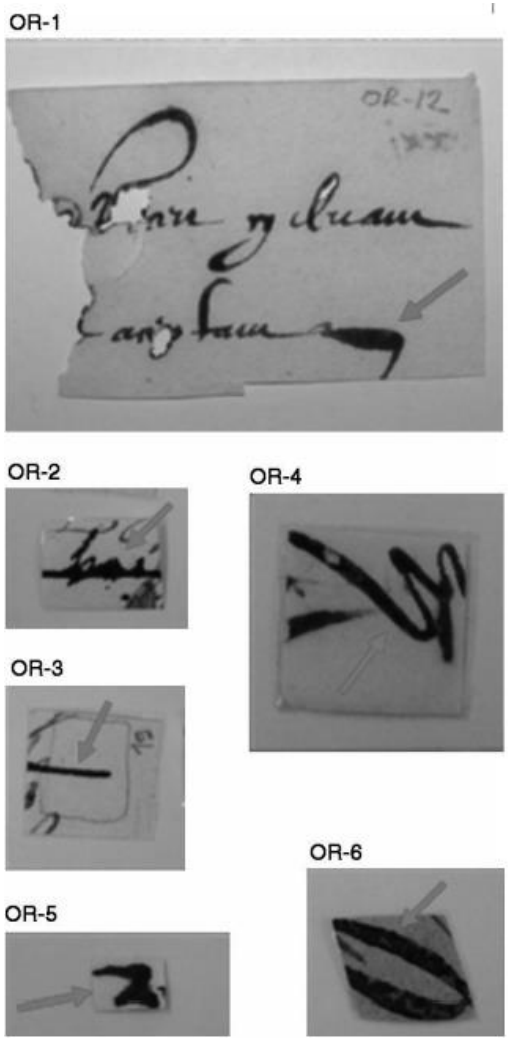
- Fe and Mn k-edge XANES study of ancient Roman glasses

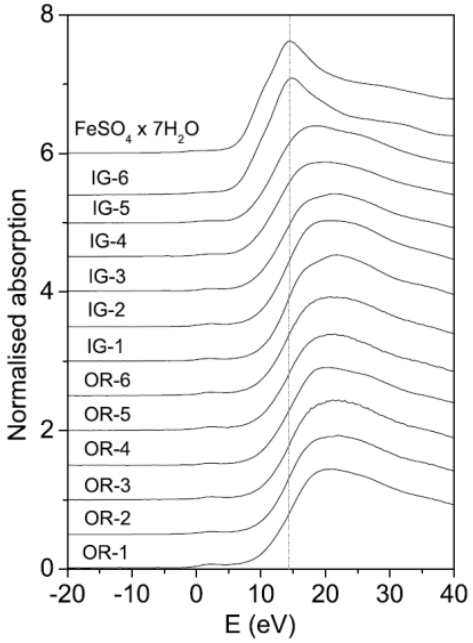
Fragments of perfume bottles (2nd century AD)

S. Quartieri et al., Eur. J. Min. (2002) 14(4),749-756



- XANES analysis of Fe valence in iron gall inks





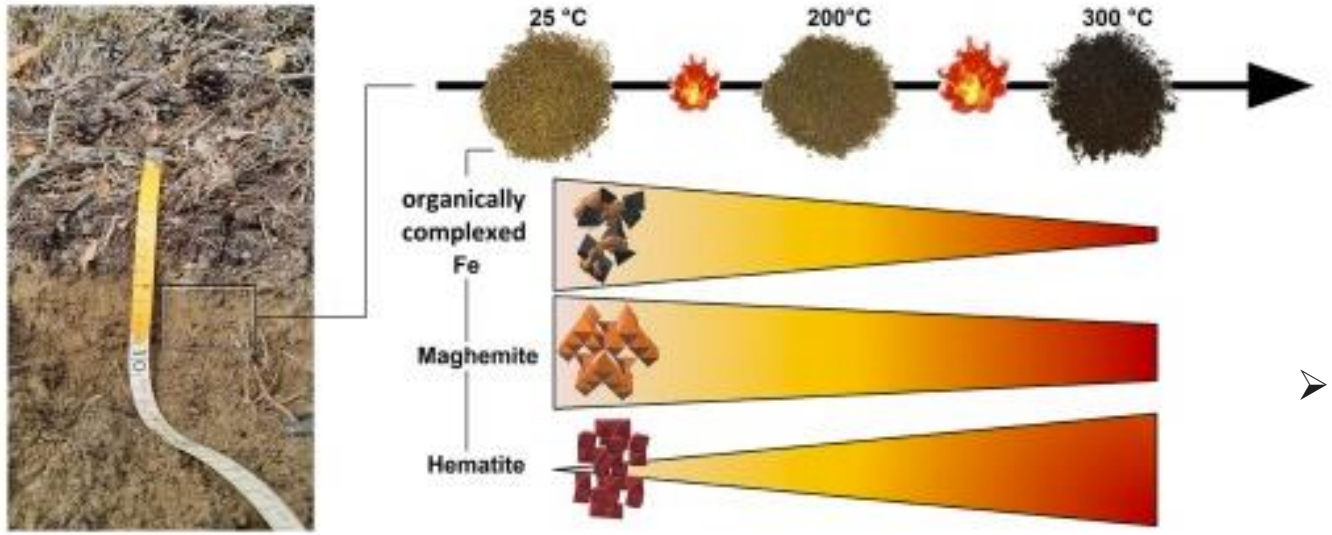
Application 4: Environmental Science

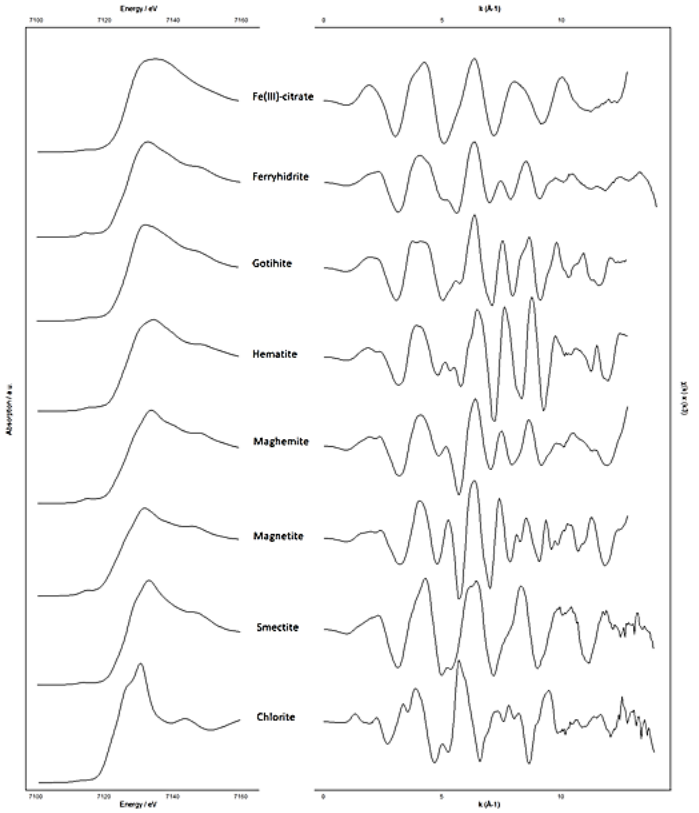
Forest soils

Geoderma
Volume 444, April 2024, 116858

Fire simulation effects on the transformation of iron minerals in alpine soils

Sara Negri [a], Beatrice Giannetta [a b], Jessica Till [c], Danilo Oliveira de Souza [4], Daniel Said-Pullicino [a], Eleonora Bonifacio [a]





- The heat-induced modifications in Fe species and organic compounds did not promote the stabilization of the remaining OM (organic matter), highlighting the weak nature of soil organo-mineral associations in an after-fire scenario.

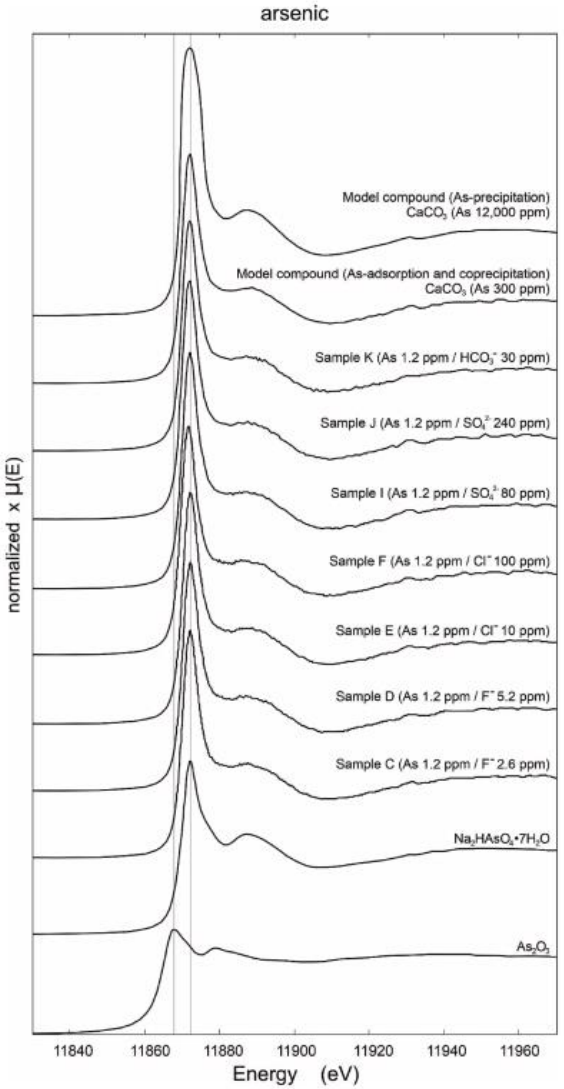
Application 4: Environmental Science

Applied Geochemistry
Volume 156, September 2023, 105762

An identification of arsenic retention mechanisms in column filtration systems packed with limestone

Antonio Salvador Sosa Islas [a], María Aurora Armienta Hernández [b], René Loredo Portales [c], Alejandra Aguayo Ríos [b], Olivia Cruz Ronquillo [b]

The high concentrations of arsenic in the groundwater of Zimap´an, Hidalgo, Mexico, have led to the search for options that contribute to resolving this problem.



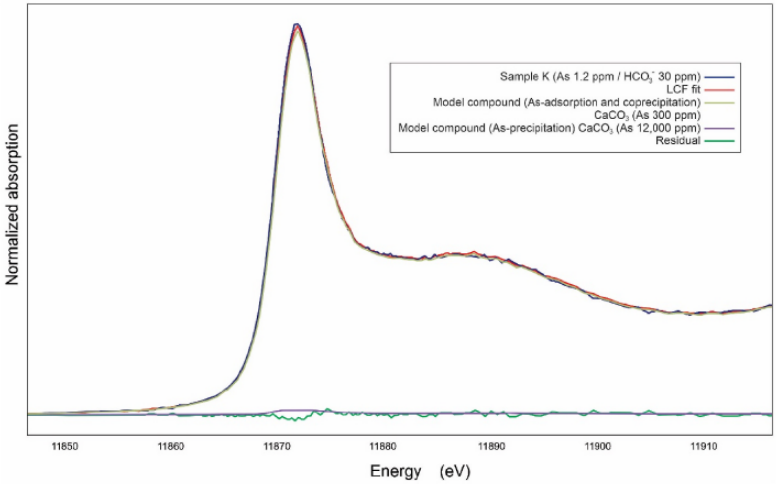


Fig. 3. Arsenic linear combination fitting method (LCF) for sample K (As 1.2 ppm and HCO_3^- 30 ppm).

- The mechanisms of arsenic removal by calcite, the limestone's main constituent was studied by XAS.
- The main processes of arsenic retention in calcite are adsorption (forming corner-sharing inner-sphere surface complexes) and coprecipitation (replacing AsO_4 in the carbonate site).

More Information

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XAFS home | Contacts | Research | Beamline description | Specifications | Information for users | Safety at XAFS

XAFS

Welcome to XAFS at Elettra

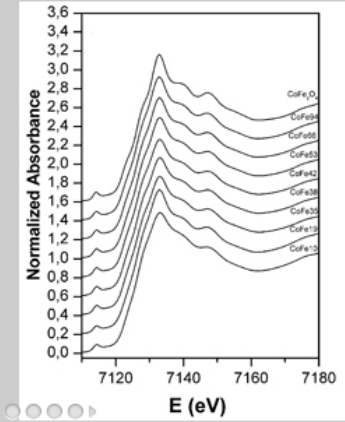
XAFS at Elettra is the Italian beamline dedicated to x-ray absorption spectroscopy. It is installed on a bending magnet source and it was designed to cover a **wide energy range: from 2.4 to 25 keV** . In addition, different collection modes and sample environments are available (including furnace, liquid-N_2 cryostat and cells for liquid samples). In this way XAFS beamline meets the needs of a large number of researchers in the area of conventional x-ray absorption spectroscopy.
For this reason the research activity at the XAFS at Elettra is quite diverse and ranges from fundamental physics to catalysis to material and environmental science.

Research highlights | Publications | Calendar

Exploring the Effect of Co Doping in Fine Maghemite Nanoparticles

Nanosized spinel ferrites are the subject of increasing interest in the current landscape of nanotechnology due to their remarkable properties that make them suitable for a large range of applications, from catalysis to biomedicine. In C-substituted ferrite nanoparticles, XAFS allowed to investigate the Co ion distribution inside the lattice and to exclude the unexpected magnetic behaviour arises from differrent metal ion distribution.
E. Fantechi *et al.*, J. Phys. Chem. **116**, 8261 (2012).

Read More



Contacts

Contacts , Useful Numbers , All Pages

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XAFS Beamline Staff:

in presenza

Giuliana AQUILANTI
(Beamline Coordinator)

Email: giuliana.aquilanti@elettra.eu
Work: 8617 (ES4 P1 016)
Work: 8433 (SX PT XAFS)
Work: 8561 (SX PT XRF)
Mobile: 3351528437 (Cod. breve #89793)

in presenza

Luca OLIVI
(Beamline Scientist)

Email: luca.olivi@elettra.eu
Work: 8023 (ES4 P1 017)
Work: 8433 (SX PT XAFS)
Mobile: 3351272672 (Cod. breve #89542)

in presenza

Giovanni AGOSTINI
(Beamline Scientist)

Email: giovanni.agostini@elettra.eu
Work: 8604 (ES4 P1 014)

in presenza

Min LI
(Post Doc Knowskite-X)

Email: min.li@elettra.eu
Work: 8785 (ES4 P1 012)

in presenza

Riccardo GRISONICH
(Beamline Technician)

Email: riccardo.grisonich@elettra.eu
Work: 8034 (ES4 P1 008)
Work: 8726 (ES4 PT 010)
Work: 8716 (ES4 PT 009)
Work: 8433 (SX PT XAFS)
Work: 8917 (EHF PT TiMEx)
Work: 8561 (SX PT XRF)
Mobile: 3346492959 (Cod. breve #89467)

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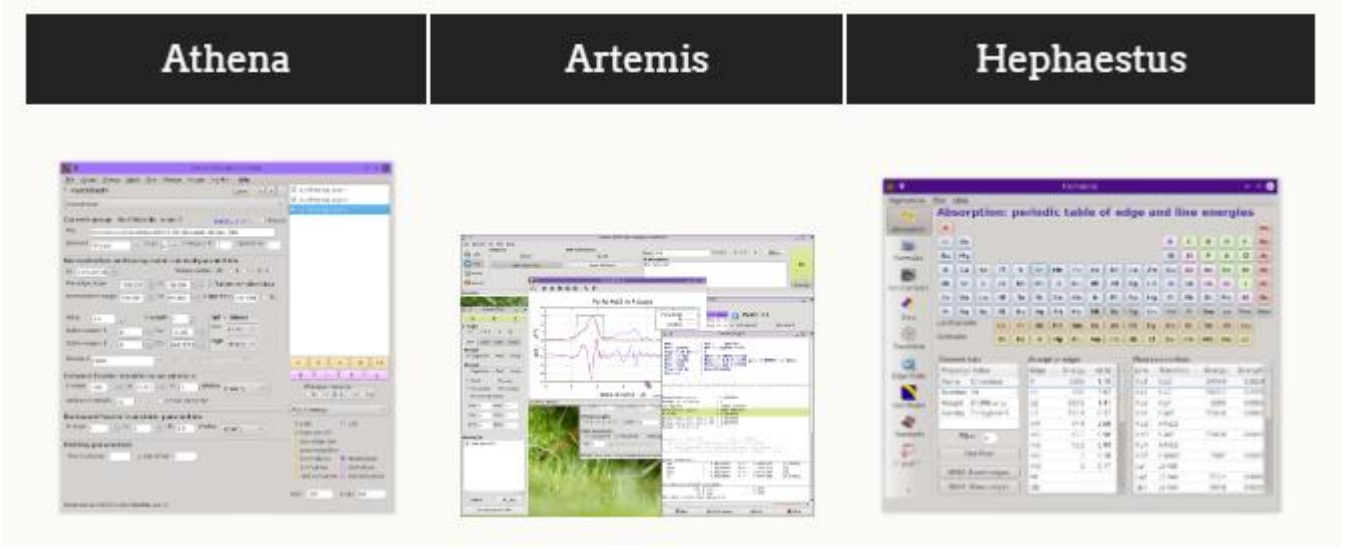
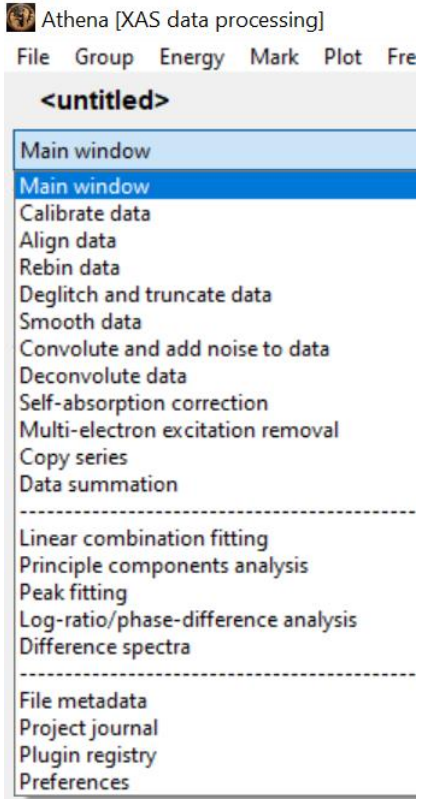
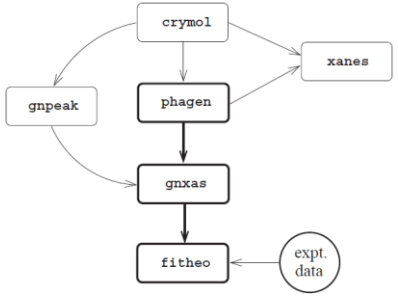
XAS Data Analysis

- XANES data analysis -Demeter （Athena） https://bruceravel.github.io/demeter/

- EXAFS data analysis -Demeter （Artemis / GNXAS software package） http://gnxas.unicam.it/pag_gnxas/redbook/orderform.html







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Thank you so much for your attention !!