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Applications of XAS to Materials Science and Cultural Heritage

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Materials science

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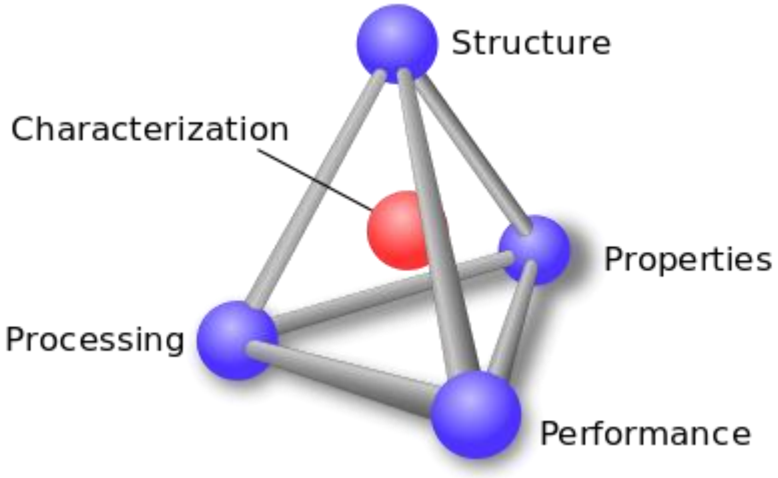
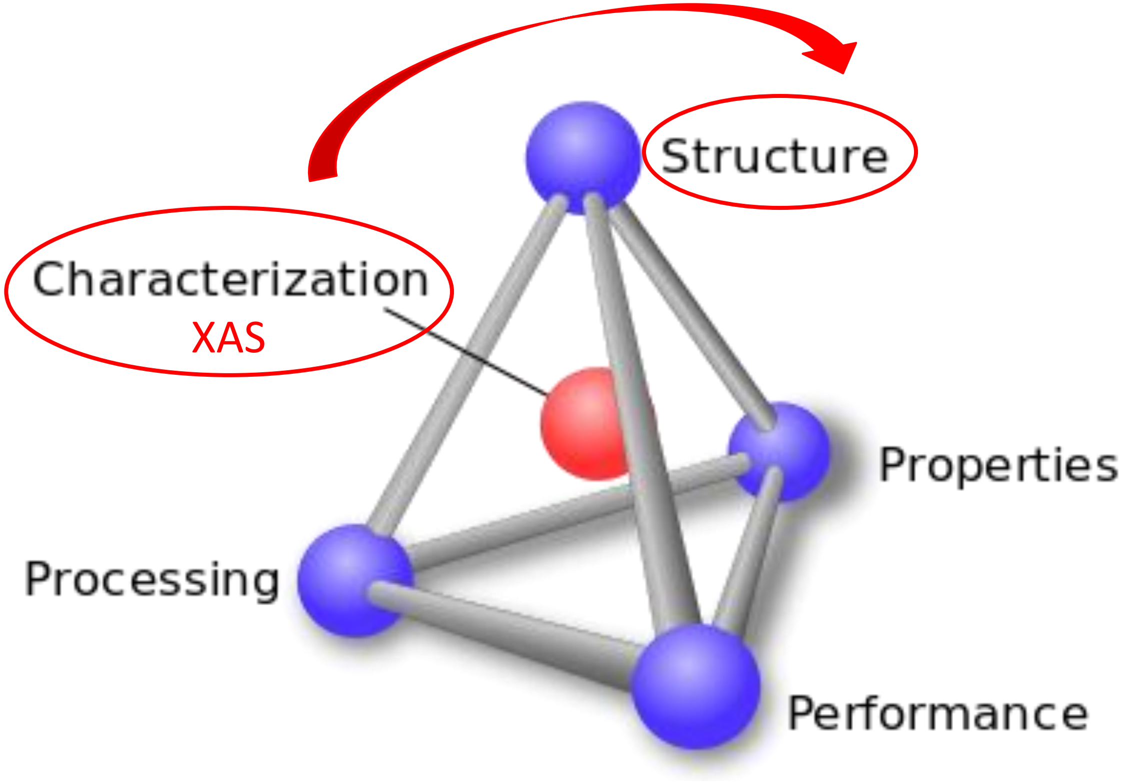
Materials science

From Wikipedia, the free encyclopedia

- The interdisciplinary field of **materials science**, also commonly termed **materials science and engineering**, involves the discovery and design of new materials, with an emphasis on solids.
- Materials science is a syncretic discipline hybridizing metallurgy, ceramics, solid-state physics, and chemistry. It is the first example of a new academic discipline emerging by fusion rather than fission.
- Materials scientists emphasize understanding how the history of a material (its *processing*) influences its structure, and thus the material's properties and performance. The understanding of processing-structure-properties relationships is called the materials paradigm.



XAS and Materials science



Advantages of XAS for Materials Science

- **Atomic selectivity**: only the structure around the atomic species chosen via the excited absorption edge is determined.
- **Applicability to ordered or disordered matter**: the fine structure originates from photoelectron scattering within at most 1 nm from the absorbing atom so that long range ordered crystals, highly structurally disordered clusters or intermediate aggregation states can be studied within the same interpretative framework.
- **A very high distance resolution** (even 0.001Å in the first coordination shell), obtainable from high quality EXAFS data.
- **Sensitivity to the local site symmetry and three dimensional atomic arrangement** (e.g. whether the selected atom is in a tetrahedral, octahedral or other symmetry site), obtainable from analysis of XANES and /or “pre-edge” spectral features.
- **Sensitivity to oxidation state and valence**, available in many cases from the energy position of the absorption edge and / or a study of the lineshape of “pre-edge” features.
- **Sensitivity to electronic structure**, available through an interpretation of the XANES lineshape in terms of the site and symmetry projected local density of unoccupied electronic states.
- **Applicability to the study of very dilute atomic species** (e.g. dopants and impurities) and extremely **thin surface** layers, possible thanks to specific experimental detection modes and set-ups.
- **High resolution in measurement of the relative atomic displacements**, which can be used to probe vibrational properties or local disorder effects.
- **Possibility of probing structure along given directions** thanks to the linear polarization of the x-ray beam and the vectorial character of the dipole matrix element.
- **Micron or sub-micron lateral spatial resolution**, available on specially designed beamlines.
- **Time resolutions** ranging from 100’s of ps (storage ring sources) to 10’s of fs (new free electron lasers), available on specialized beamlines.

F. Boscherini, from Synchrotron Radiation Basics, Methods and Applications, Springer 2015

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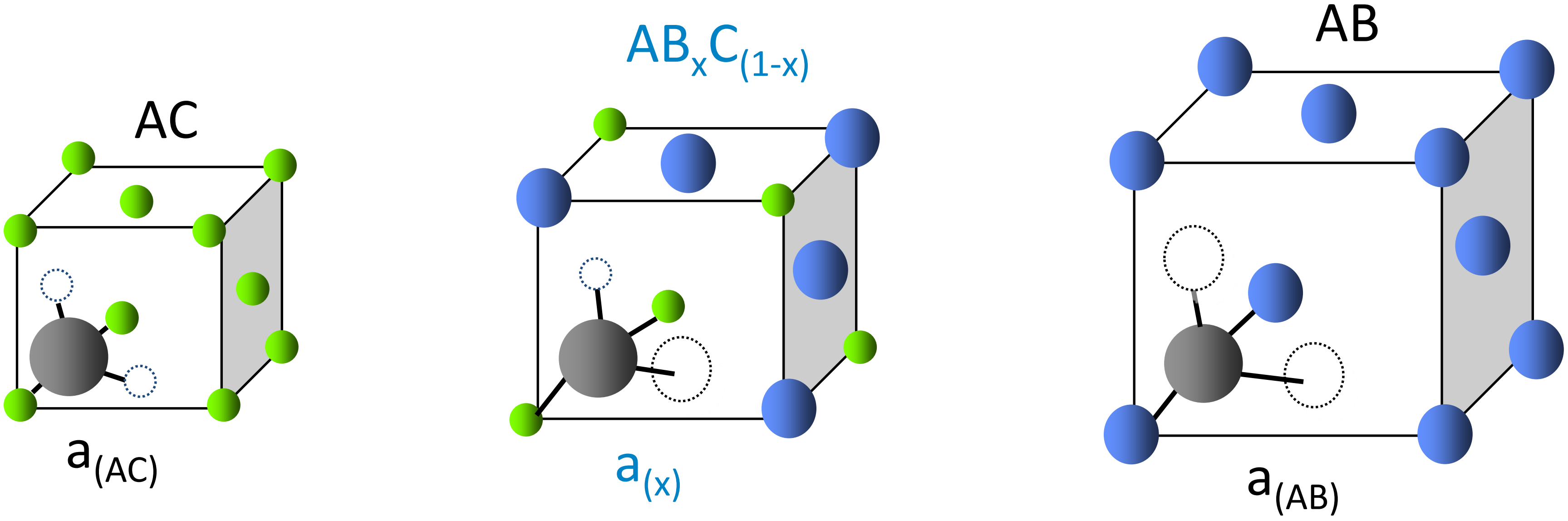
Atomic scale structure in solid solutions

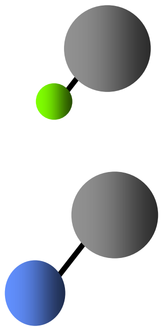
Vegard's law

Linear relation between the crystal lattice parameters of an alloy and the concentration of the constituent elements

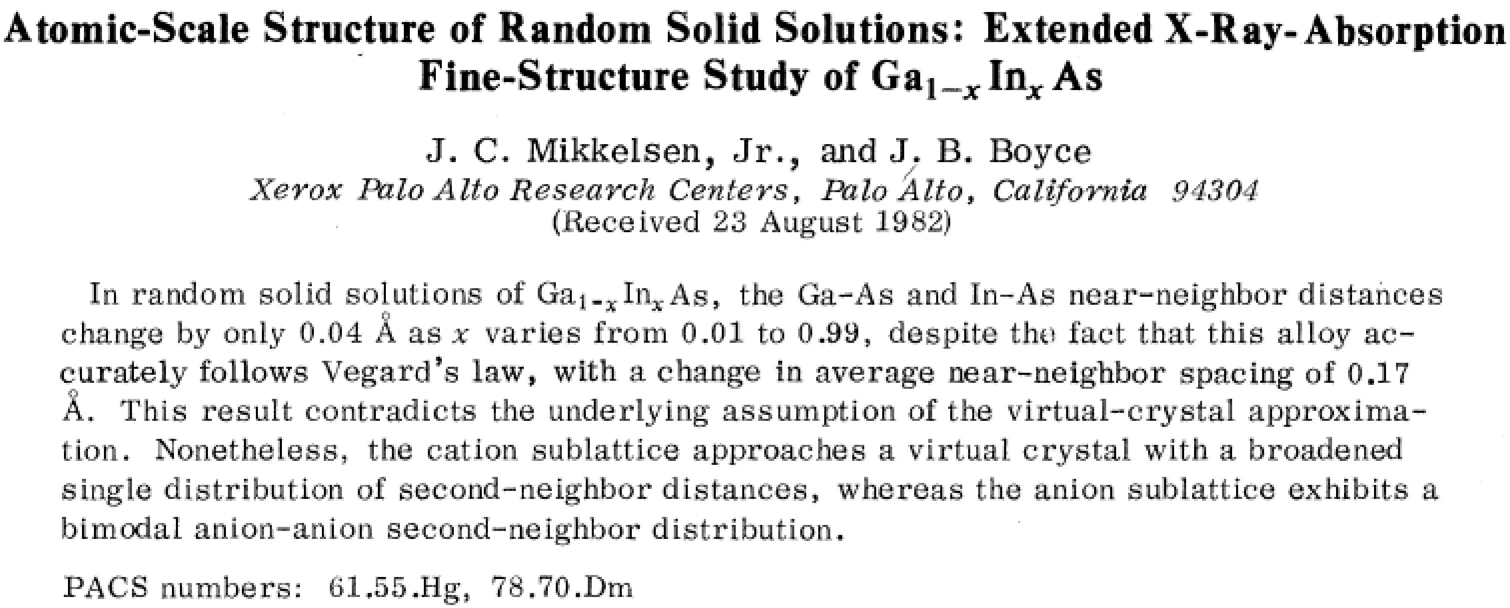


$$a_{(x)}=xa_{(AB)}+(1-x)a_{(AC)}$$

If $\left.\begin{cases} R^0_{(AC)}=(\sqrt{3}/4)a_{(AC)} \\ R^0_{(AB)}=(\sqrt{3}/4)a_{(AB)} \end{cases}\right\}$ then $R_{(AC)x}=R_{(AB)x}=(\sqrt{3}/4)a_{(x)}$



Virtual crystal approximation



Atomic-Scale Structure of Random Solid Solutions: Extended X-Ray-Absorption Fine-Structure Study of $Ga_{1-x}In_xAs$

J. C. Mikkelsen, Jr., and J. B. Boyce
Xerox Palo Alto Research Centers, Palo Alto, California 94304

(Received 23 August 1982)

In random solid solutions of $Ga_{1-x}In_xAs$, the Ga-As and In-As near-neighbor distances change by only 0.04 Å as x varies from 0.01 to 0.99, despite the fact that this alloy accurately follows Vegard's law, with a change in average near-neighbor spacing of 0.17 Å. This result contradicts the underlying assumption of the virtual-crystal approximation. Nonetheless, the cation sublattice approaches a virtual crystal with a broadened single distribution of second-neighbor distances, whereas the anion sublattice exhibits a bimodal anion-anion second-neighbor distribution.

PACS numbers: 61.55.Hg, 78.70.Dm

$Ga_{1-x}In_xAs$ follows Vegard's law

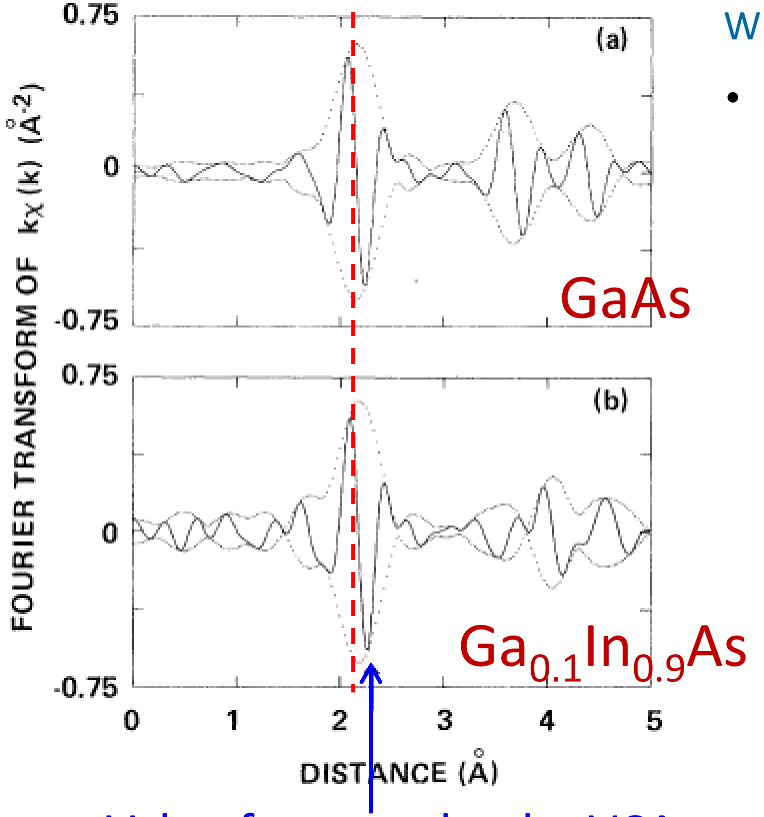
According to the VCA:

- $d_{Ga\text{-}As}=d_{In\text{-}As}$
- $\Delta d = 0.17$ for x varying from 0.01 to 0.99

For a given composition

- $d_{In\text{-}As}$ in the solid solution is closer to $d_{In\text{-}As}$ in InAs than to the value of the VCA
- $d_{Ga\text{-}As}$ in the solid solution is closer to $d_{Ga\text{-}As}$ in GaAs than to the value of the VCA

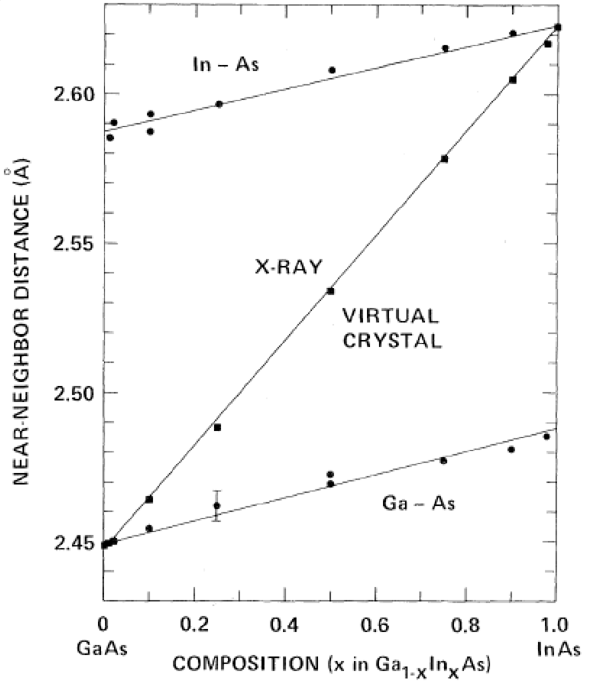
Bond lengths stay close to sum of covalent radii
Violation of VCA
First evidence of strong local structural disorder



Value foreseen by the VCA

With varying composition

- $\Delta d_{In\text{-}As}$ and $\Delta d_{Ga\text{-}As}$ change only of 0.04 instead of 0.17 as foreseen by the VCA



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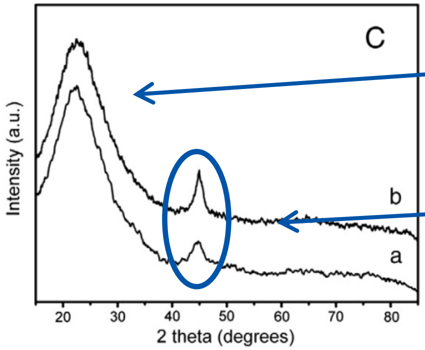
Identification on NPs

FeCo alloy NPs embedded on mesoporous silica

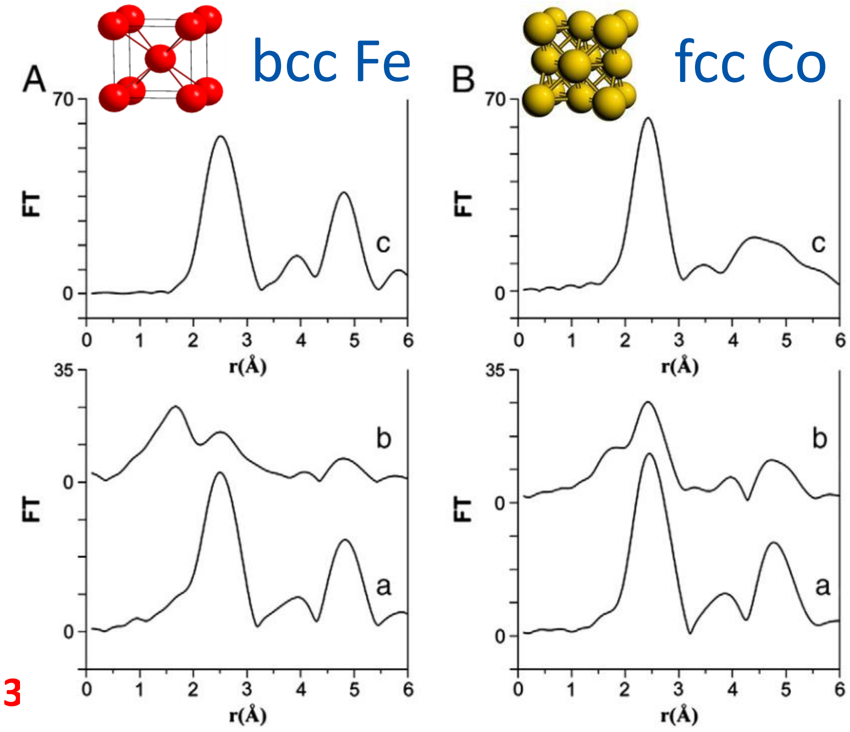


a-SiO_2

bcc Fe or bcc FeCo

Two prep methods:

a) co-precipitation
b) impregnation



bcc Fe

fcc Co

Fe K-edge

Co K-edge

Carta et al., J. of Non-Cryst. Sol. **3**

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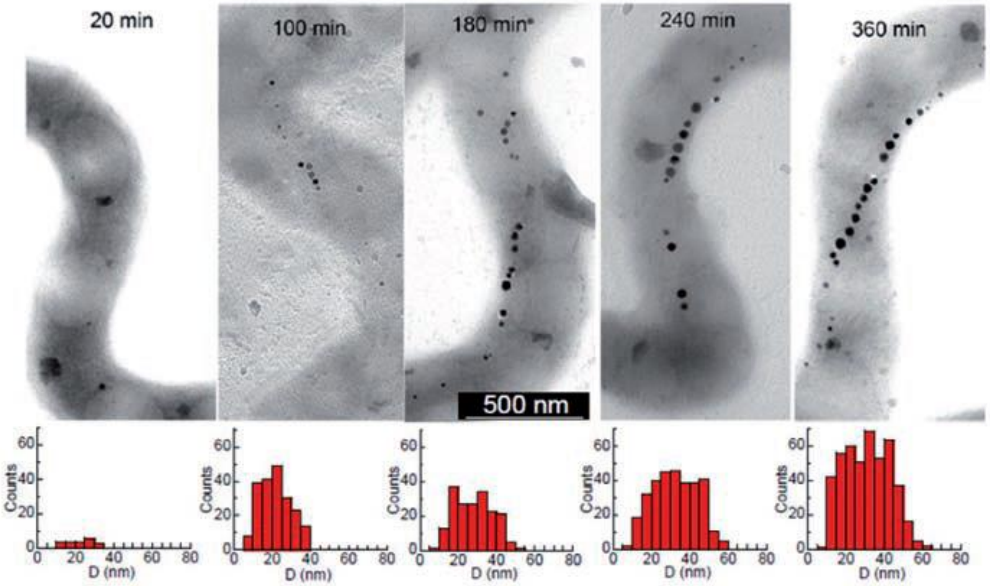
Magnetite biomineralization in bacteria

M. L. Fdez Gubieda et al., ACS Nano **7** 3297 (2013)

- Many organisms (magnetotactic bacteria) produces magnetic nanoparticles
- Magnetospirillum gryphiswaldense produces magnetite nanoparticles (biomineralization) surrounded by a lipidic membrane (magnetosomes)



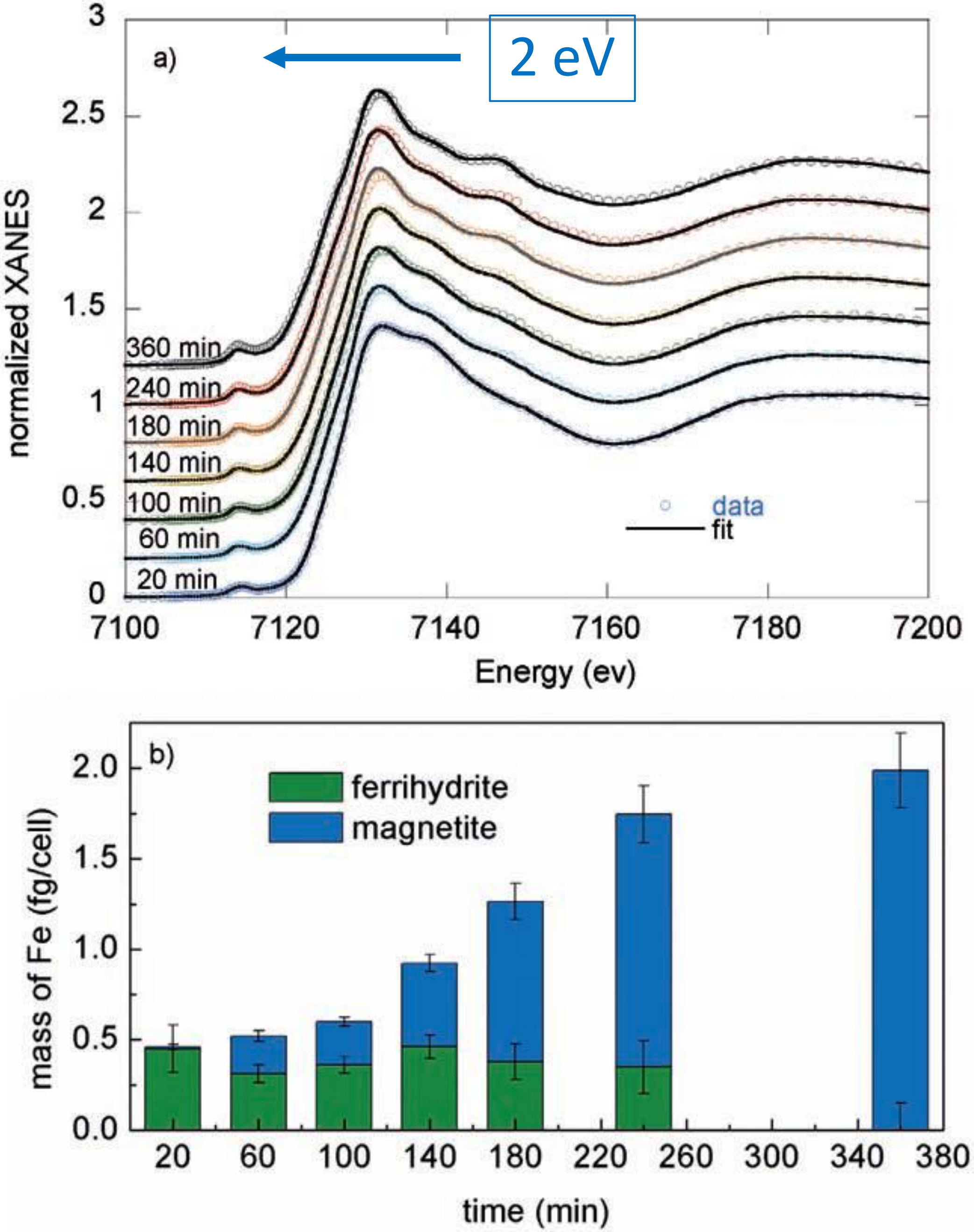
- Chaines used as compass needles to orient in the geomagnetic field
- Good biocompatibility and therefore interesting in biomedical applications
- Understanding of the biomineralization process to design new materials

Magnetite biomineralization in bacteria

M. L. Fdez Gubieda et al., ACS Nano **7** 3297 (2013)

XANES

- To identify the oxidation state and local geometry of the absorbing atom
- To identify and quantify the different Fe phases
- 2 eV shift towards lower energies
- LC of ferrihydrite (Fe^{3+}) and magnetite (Fe^{3+} and Fe^{2+})
- ferrihydrite constant and then in the end of the biomineralization process undetectable



2 eV

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SCIENTIFIC REPORTS

OPEN

Efficient artificial mineralization route to decontaminate Arsenic(III) polluted water - the Tooeleite Way

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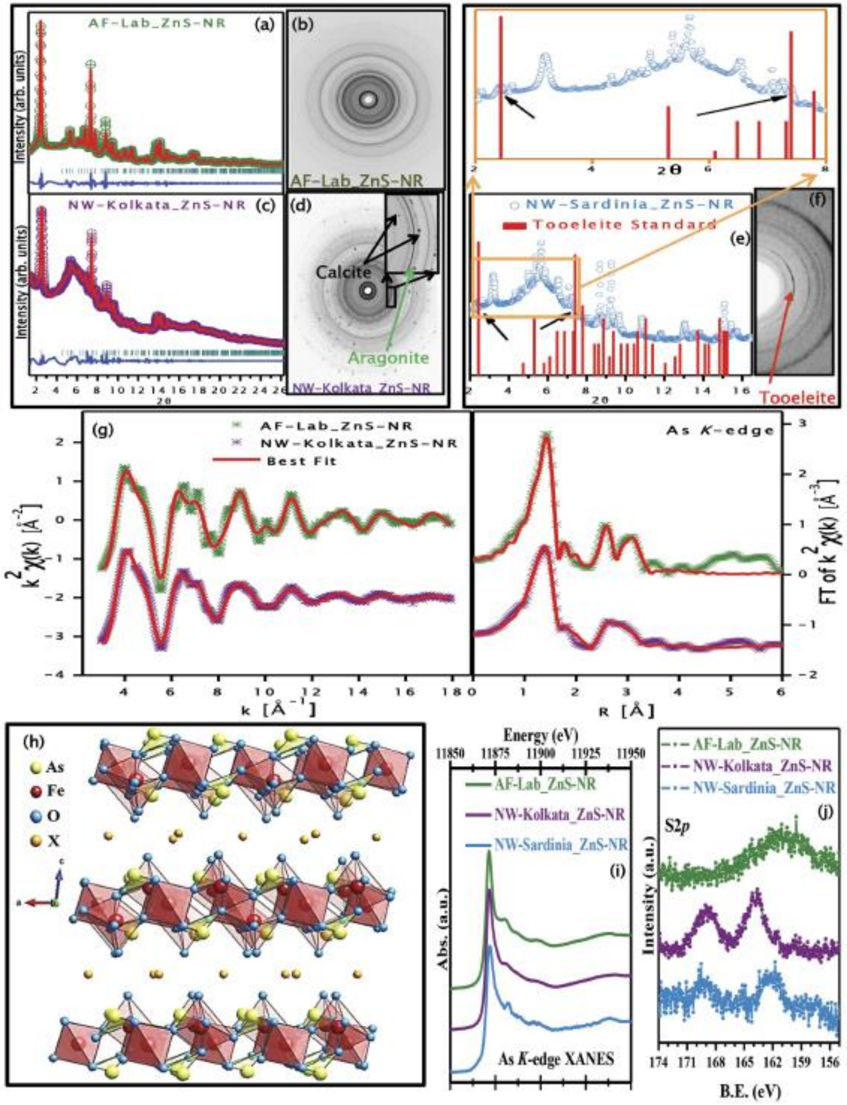
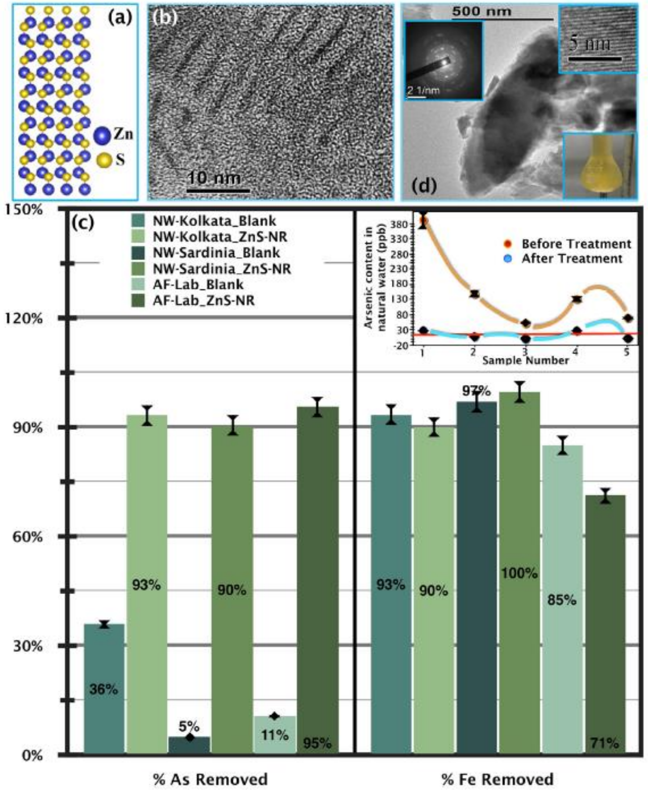
Arindam Malakar[1], Bidisa Das[2], Samirul Islam[1], Carlo Meneghini[3], Giovanni De Giudici[4], Marco Merlini[5], Yury V. Kolen'ko[6], Antonella Iadecola[7], Giuliana Aquilanti[7], Somobrata Acharya[2] & Sugata Ray[1,2]



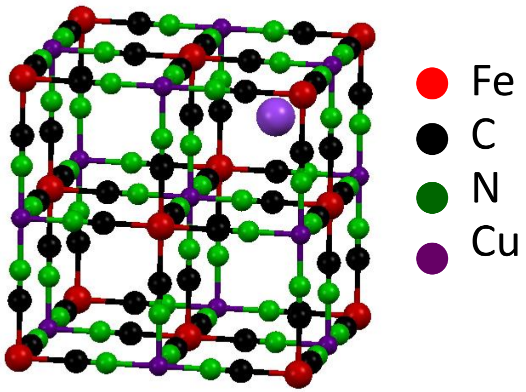


Cu^{2+}-loaded Cu hexacyanoferrate

M. Giorgetti et al., PCCP **14**, 5527 (2012),
M. Giorgetti et al., J. Phys.: Conf. Series 430, 012049 (2013)

$A_xM_y[Fe(CN)_6]\cdot zH_2O$

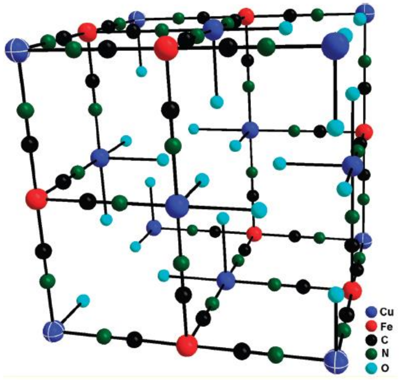
“soluble”* structure (F-43m)



- a ~ 10.2 Å
- alkaly metals occupy intertitial 8c positions
- **-CN-Cu-NC-Fe-CN-** linear chains
- Fe and Cu in octahedral sites

  6 x Fe-CN-Cu
  6 x Cu-NC-Fe

“insoluble” * structure (Pm-3m)



- Model with [**Fe**$(CN)_6]^{3-}$ ion vacancies

6 x Fe-CN-Cu
4.5 x Cu-NC-Fe
1.5 x Cu-O

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Cu^{2+}-loaded Cu hexacyanoferrate: interest

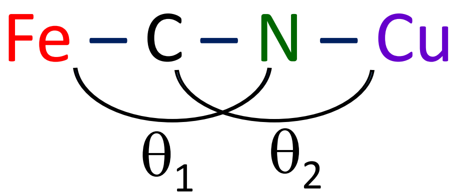
Applications

- Electrochromism
- Electrocatalysis
- Ionic and electronic conductivity
- Charge storage
- Photo-induced magnetisation
- Electro-catalytic oxidation of alcohols in alkaline medium

Aim of the study

- Relationship between structure and properties
- **Amount of vacancies linked to the ability of H storage**

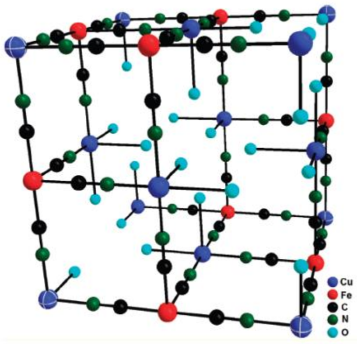
Data analysis strategy



Fe – C – N – Cu

θ_1 θ_2

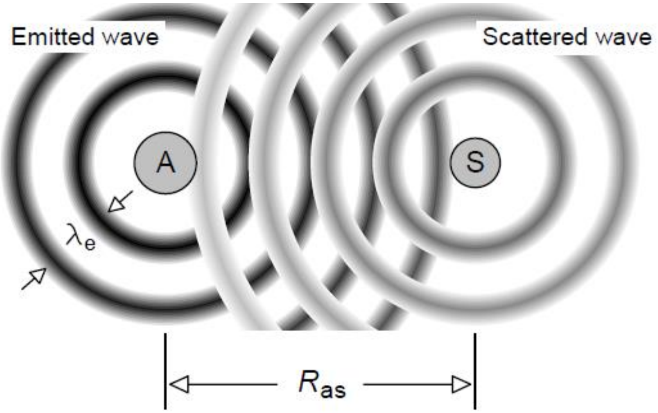
Linear chains between Cu and Fe gives rise to a *superfocusing effect* and therefore to a *large EXAFS signal*

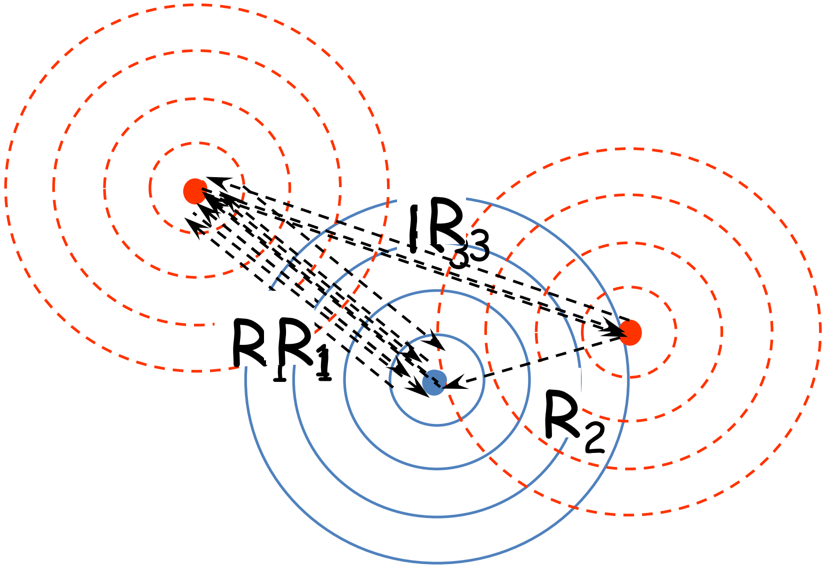


➡ Information on the amount of the vacancies

Signals for the Cu K-edge (CN)	
Two body	$\gamma_1^{(2)}$ Cu-N; (4.5)
	$\gamma_2^{(2)}$ Cu-O; (1.5)
	$\gamma_3^{(2)}$ Cu-K; (*)
Three body	$\eta_1^{(3)}$ Cu-N-C; (4.5)
Four body	$\eta_1^{(4)}$ Cu-N-C-Fe; (4.5)

Single scattering and multiple scattering





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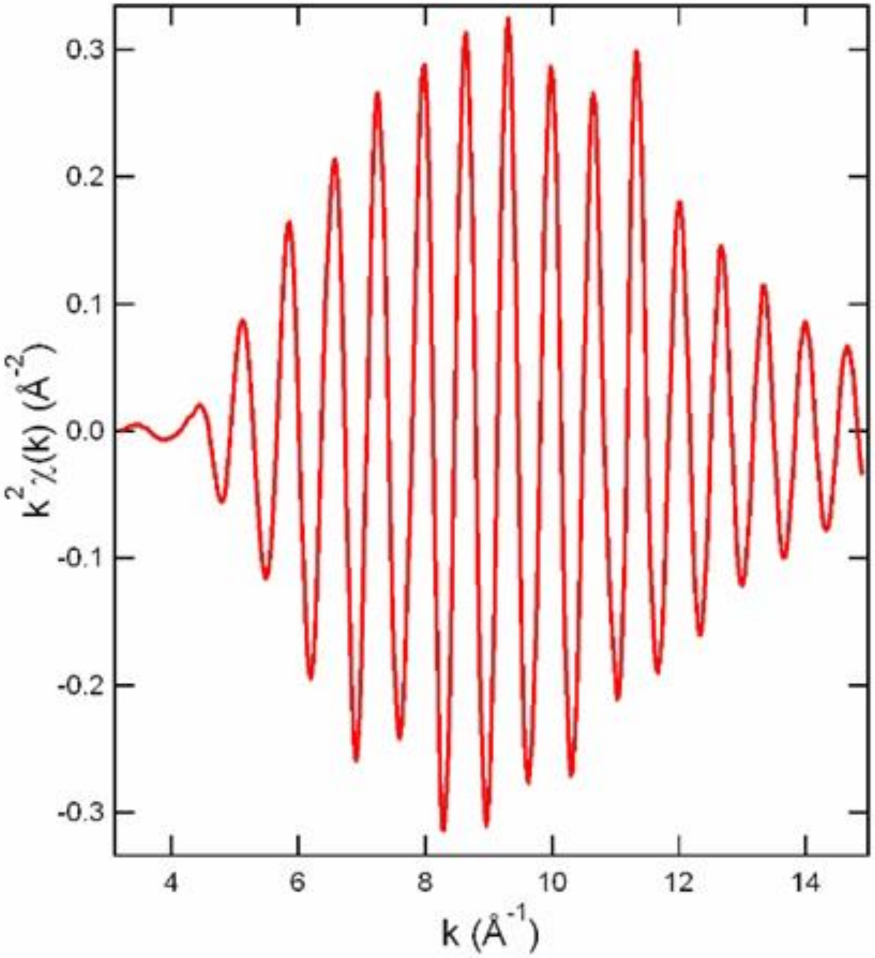
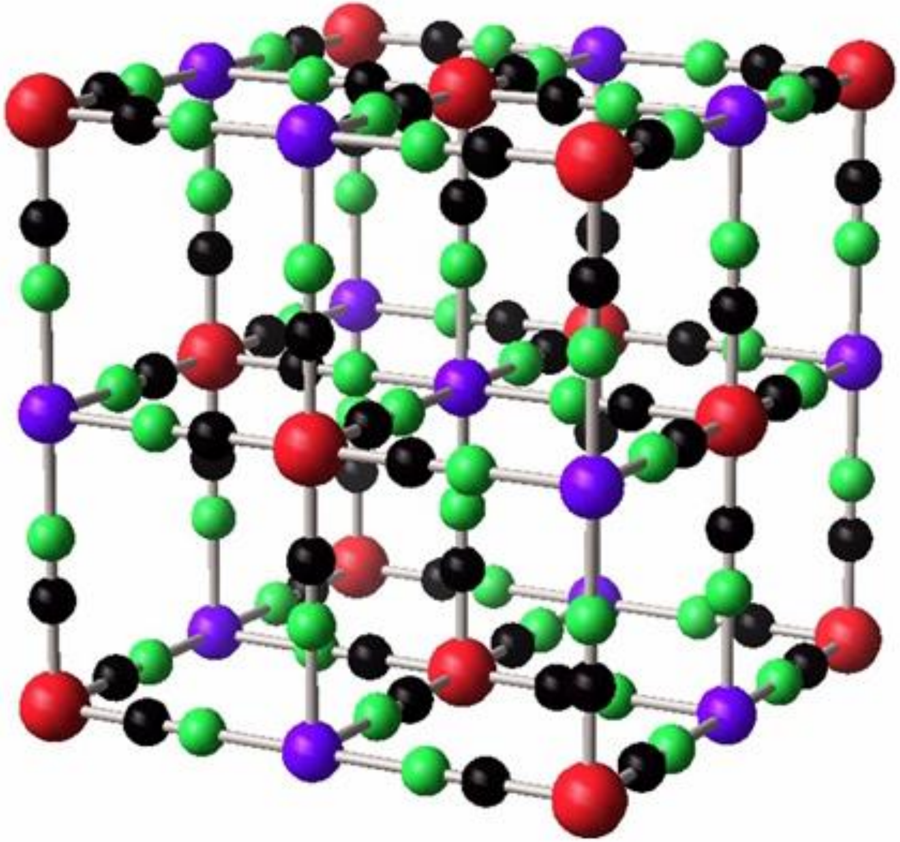
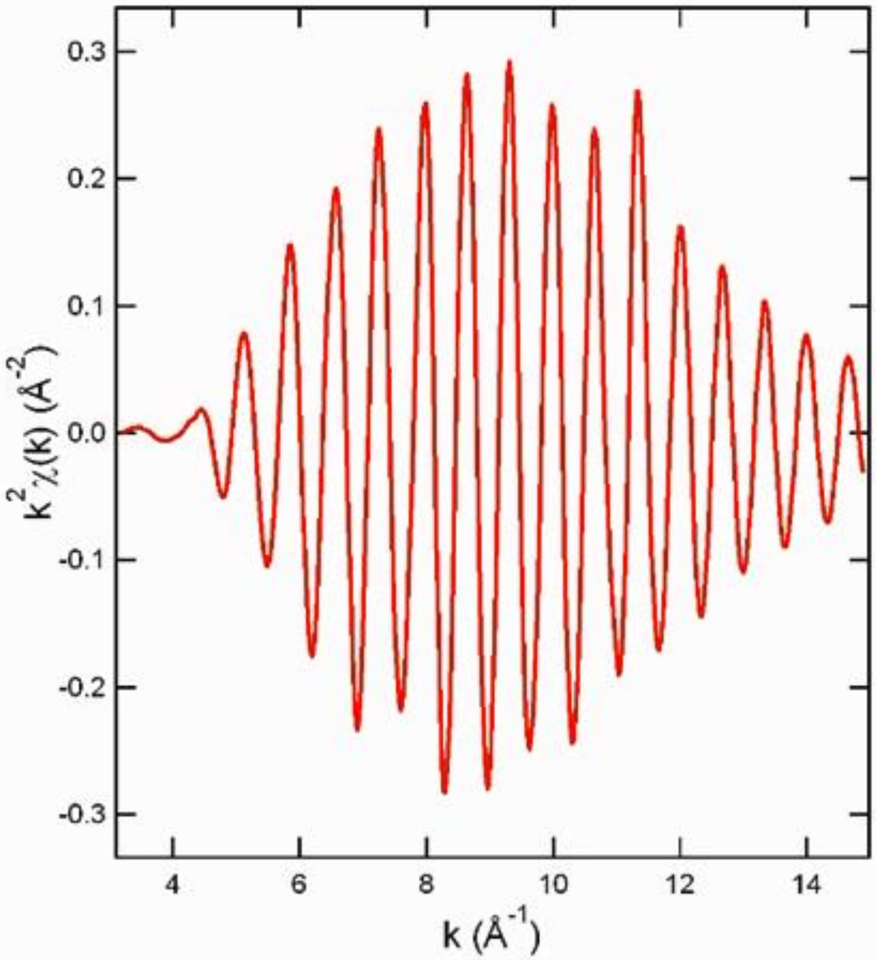
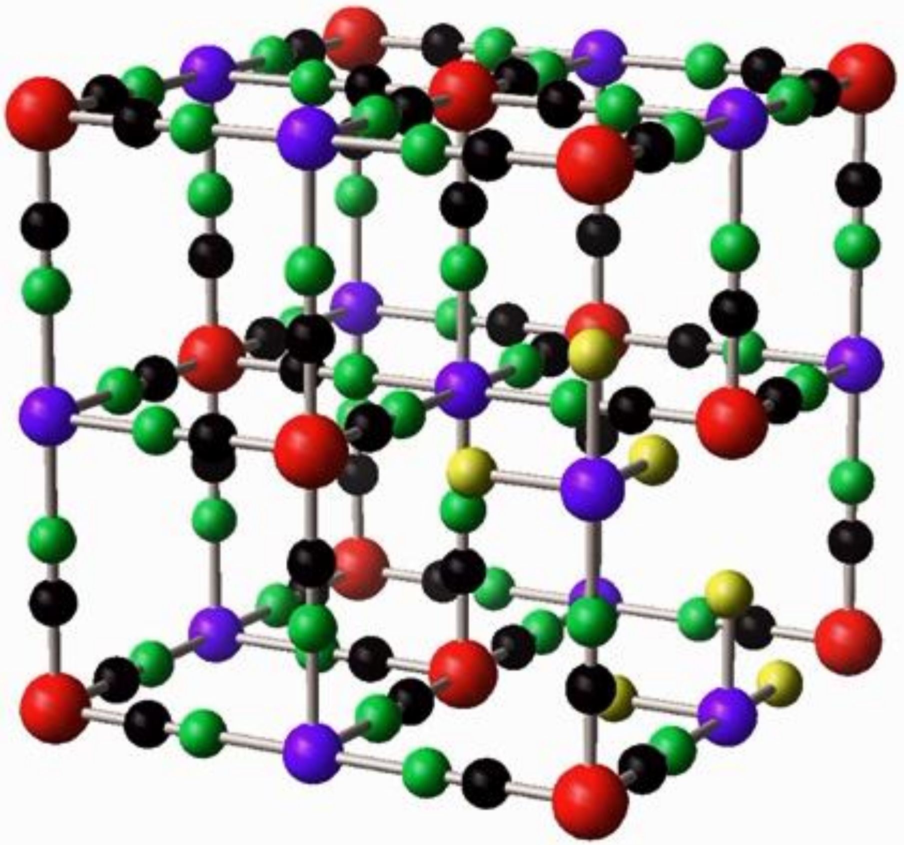
Copper Hexacyanoferrate: Fe – C – N – Cu



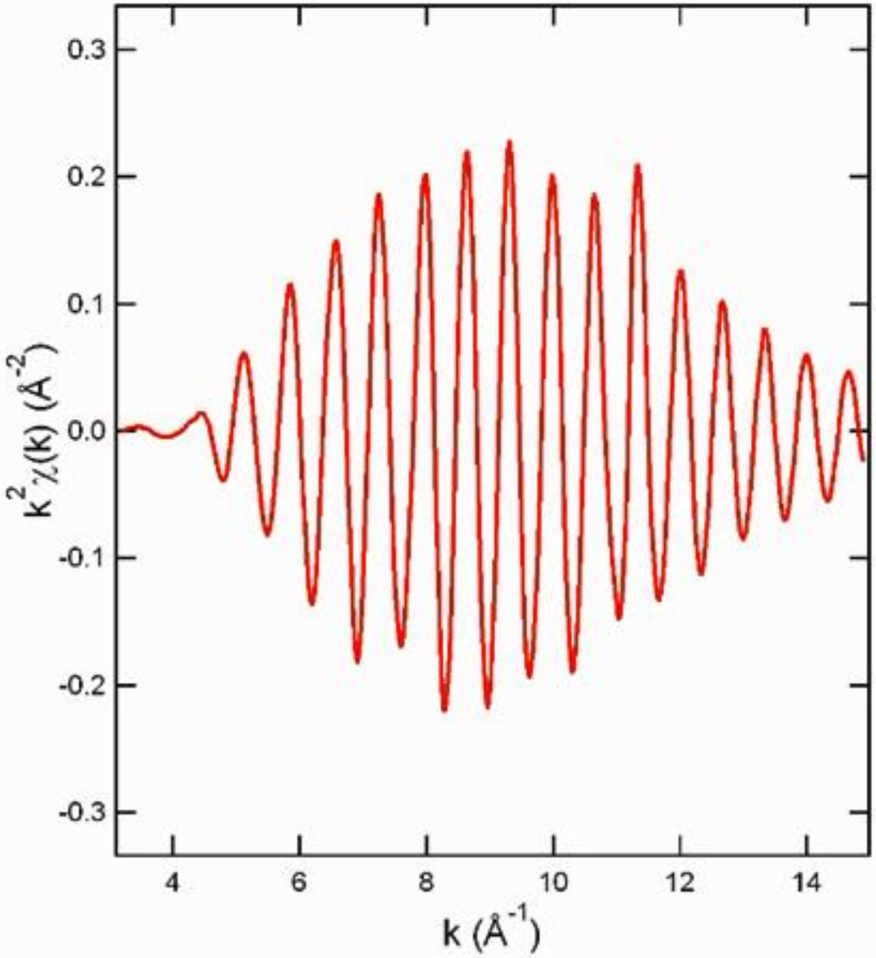


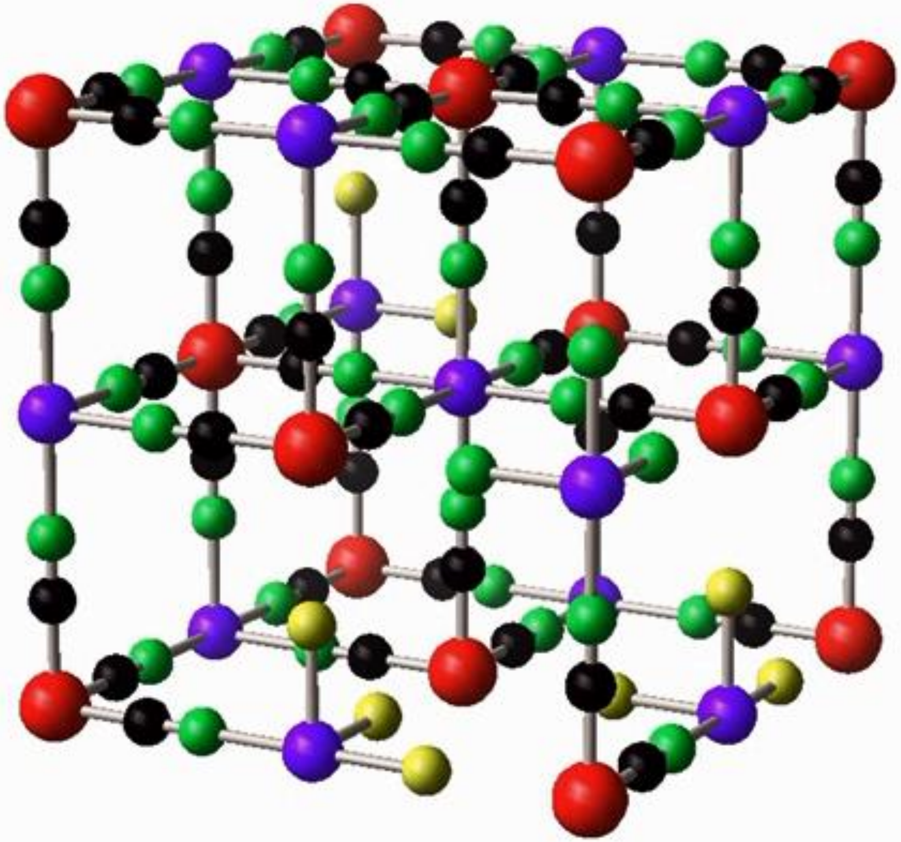
Copper Hexacyanoferrate: Fe – C – N – Cu



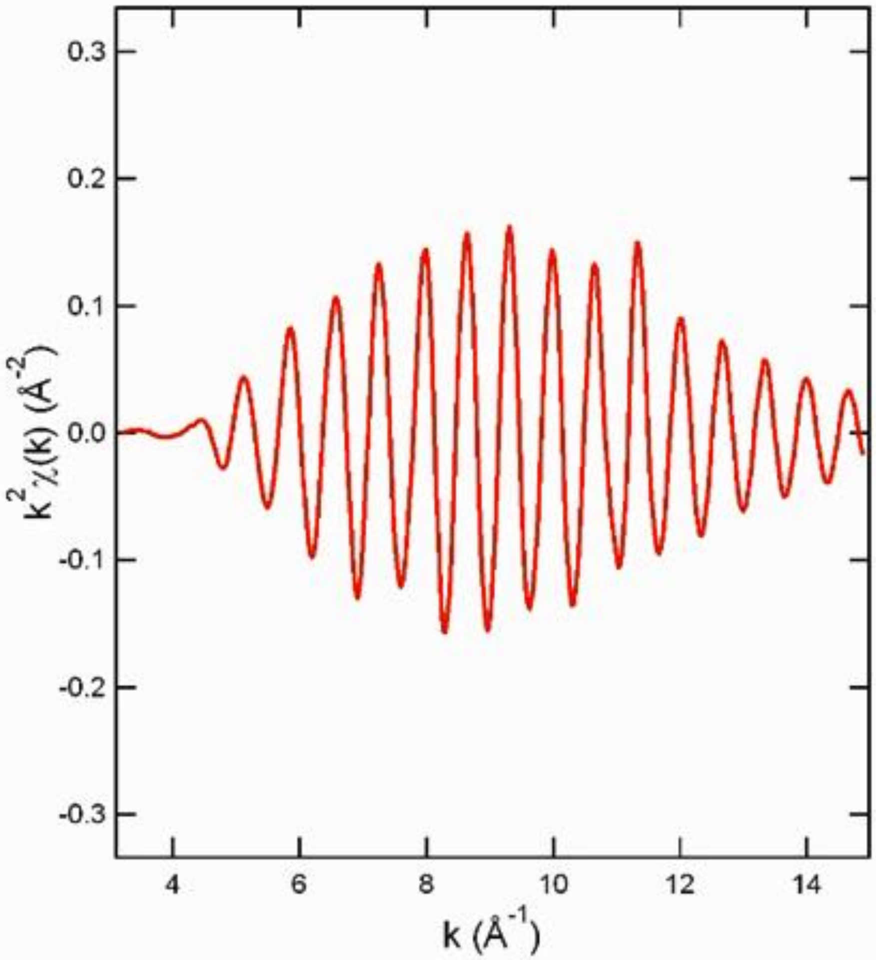


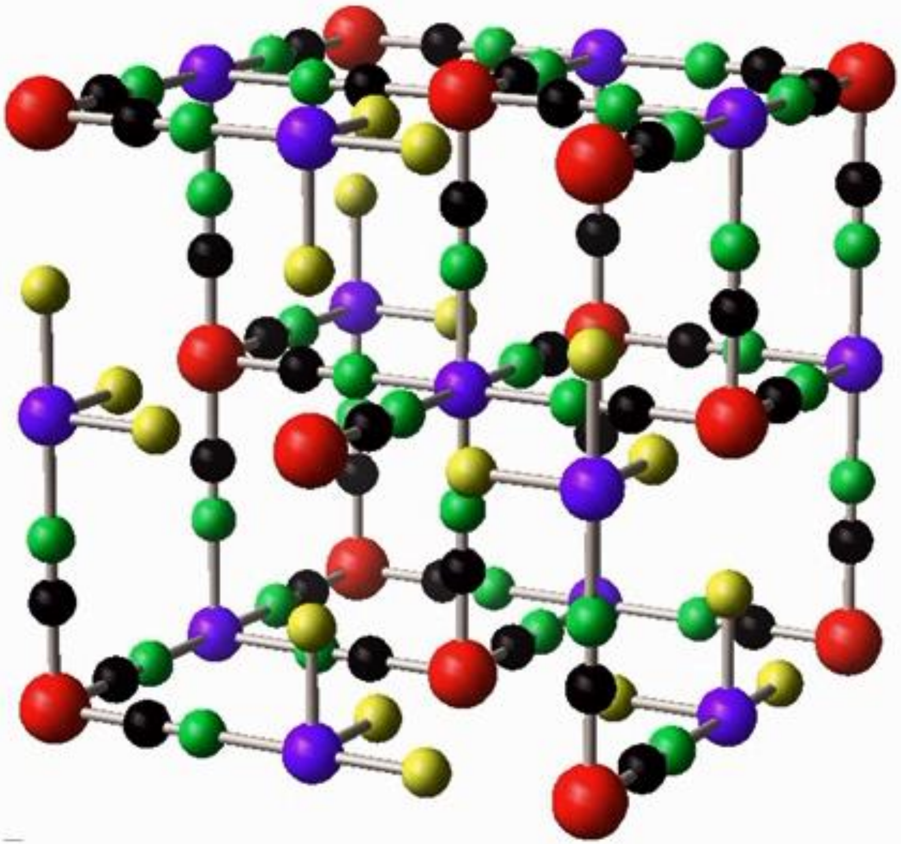
Copper Hexacyanoferrate: Fe – C – N – Cu



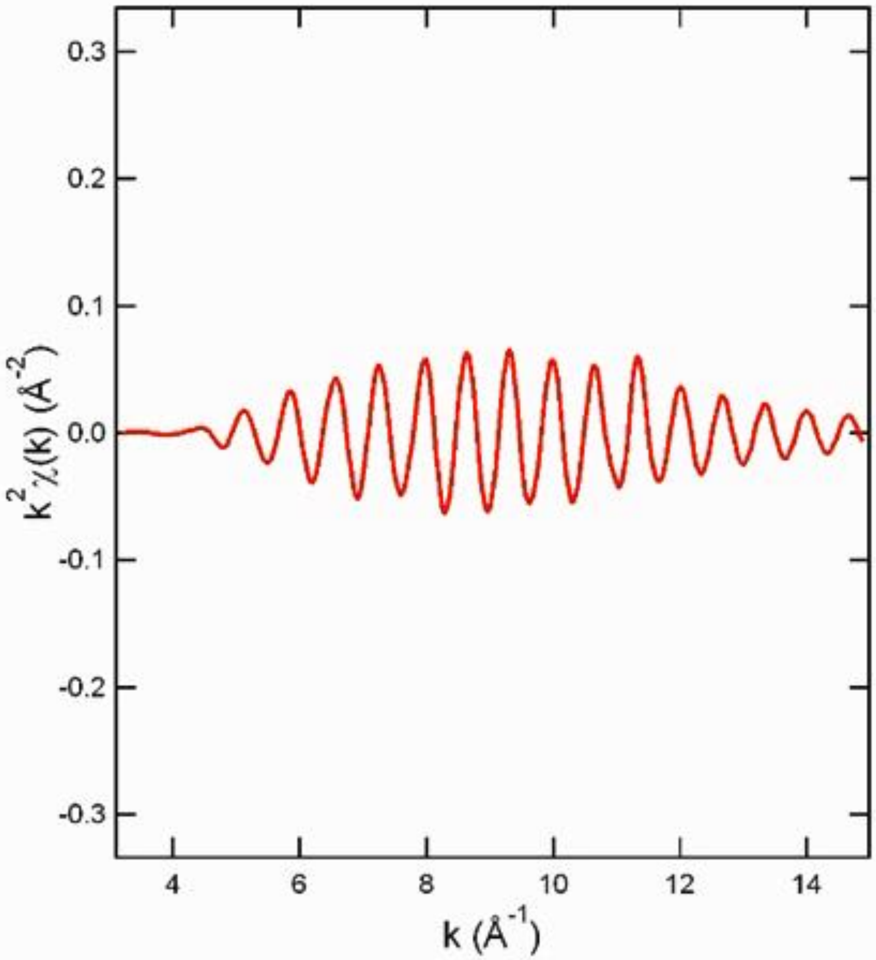


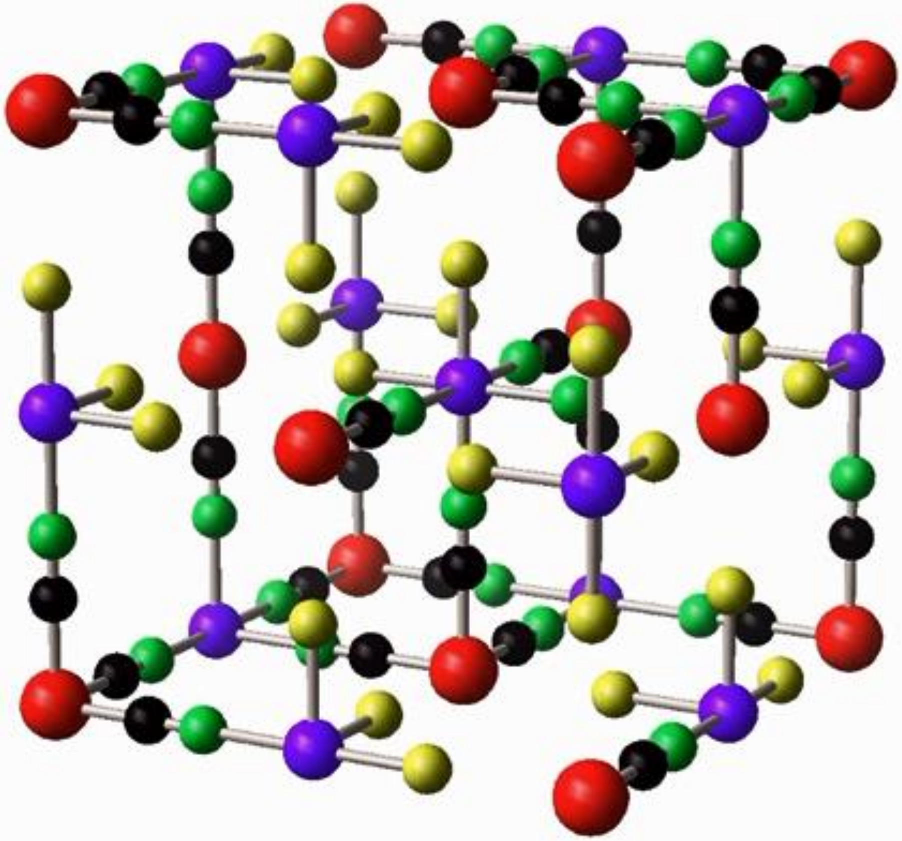
Copper Hexacyanoferrate: Fe – C – N – Cu



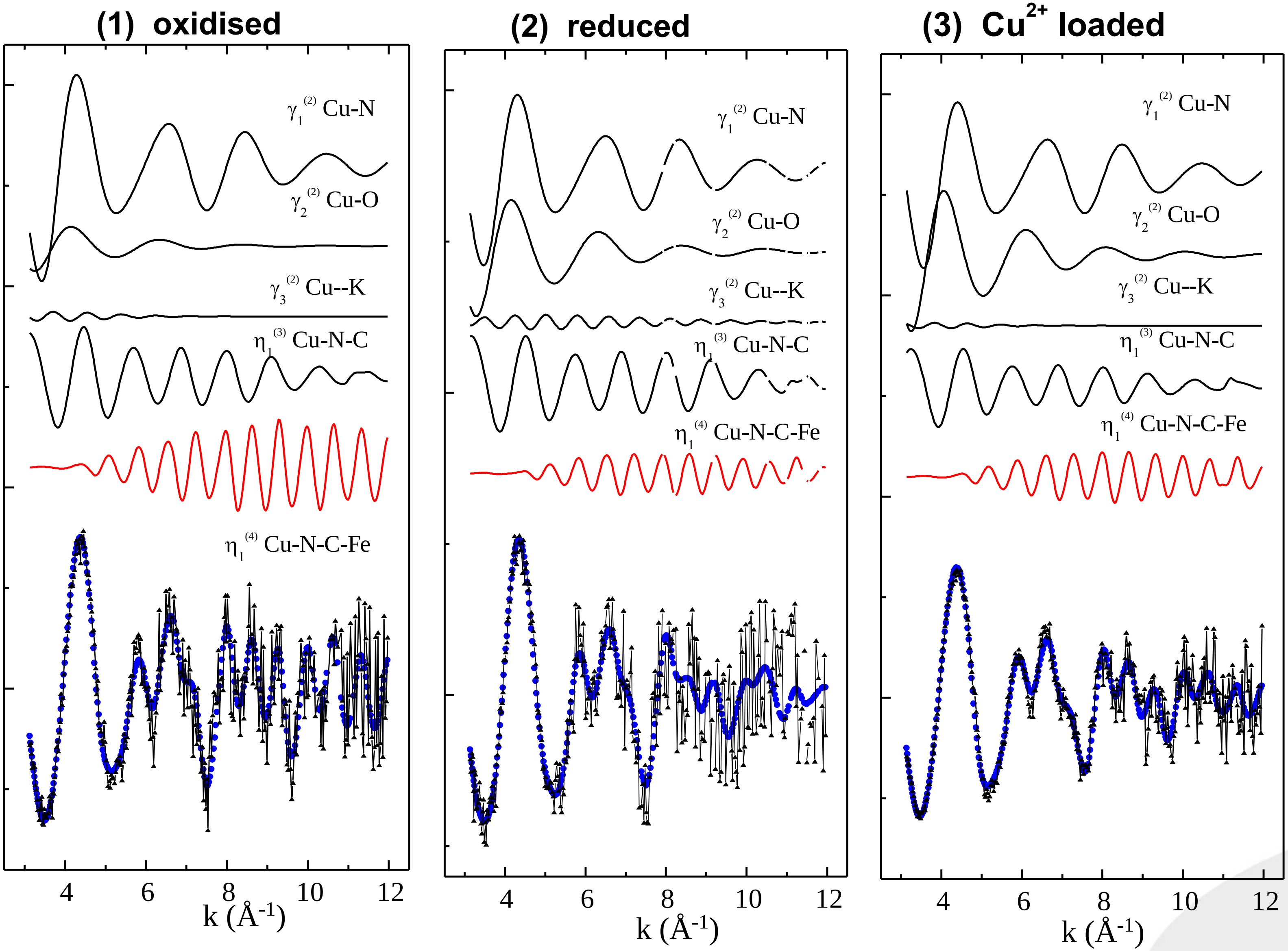


Copper Hexacyanoferrate: Fe – C – N – Cu





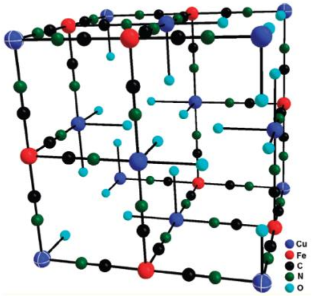
Fitting results



Ex situ -> in situ -> operando

- ***Ex situ***

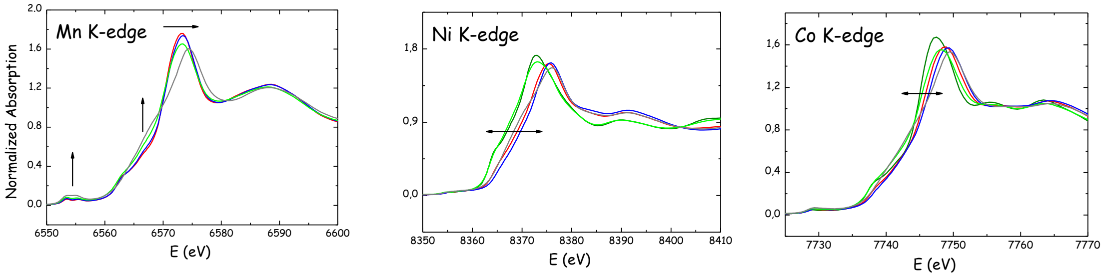
  (structural) characterization of a functional material independently of the device

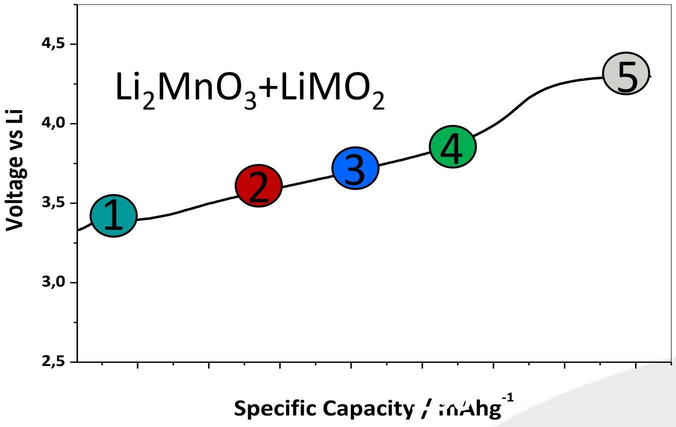


M. Giorgetti et al.,
Phys. Chem. Chem. Phys. (2012) **14**, 5527–5537

- ***In situ***

  Material is part of the device (battery, fuel cell,….) and structural characterization is done in equilibrium





M. Giorgetti, D. Wang, G. Aquilanti, D. Buchholz, S. Passerini
ChemElectroChem **2** (2015), 85

- ***Operando***

  Materials are studied under non-equilibrium real-time conditions (in operation)

Operando

- Reactions in actual batteries proceed in a non-equilibrium state
  - *operando data are expected to provide a realistic representation of the reaction behavior found under normal operating conditions*
- Typical drawbacks of ex situ experiments avoided
  - *Alterations of sensitive species because of air or moisture*
  - *relaxation reactions that may occur when opening the electric circuit*
- Operando studies can be done on a single test cell
  - *the uncontrolled differences between cells which are needed for a stepwise ex situ study of the electrochemical mechanism are suppressed*
- Possibility to check the structural and electronic reversibility of a battery system while at least one full cycle is performed.

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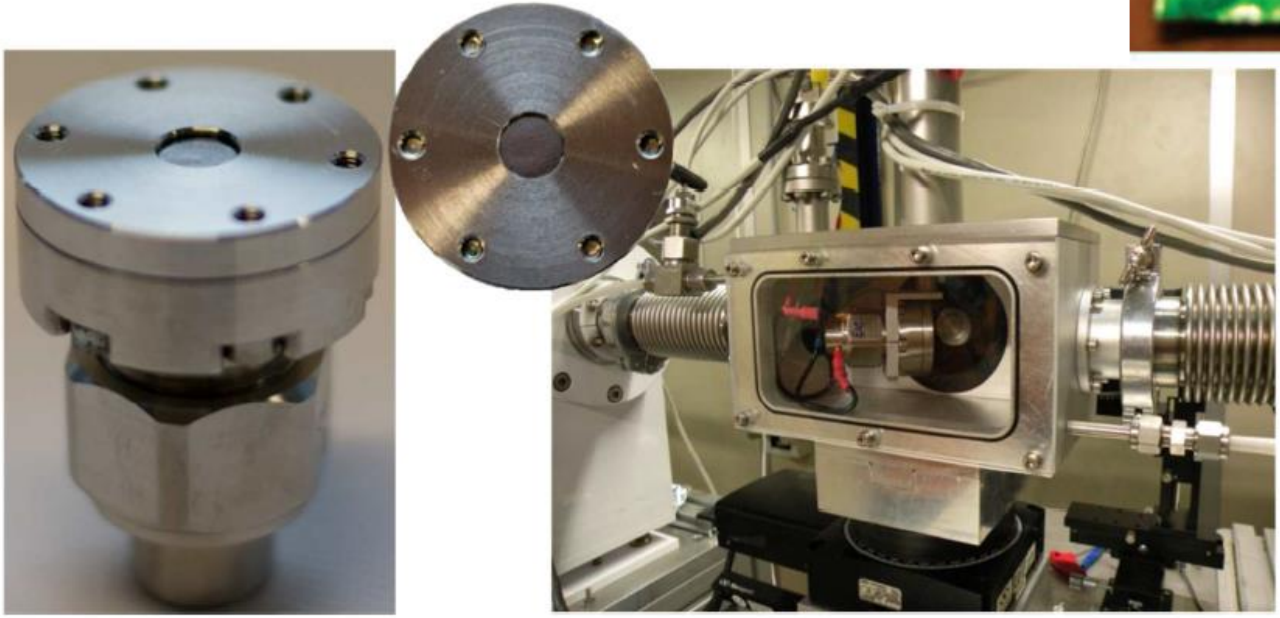
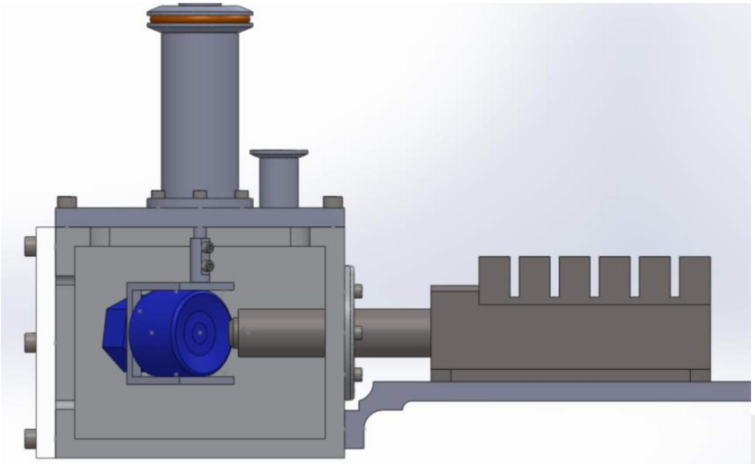
Cells and chamber





Li-S batteries

(Simplified) electrochemical reactions between Li and S:

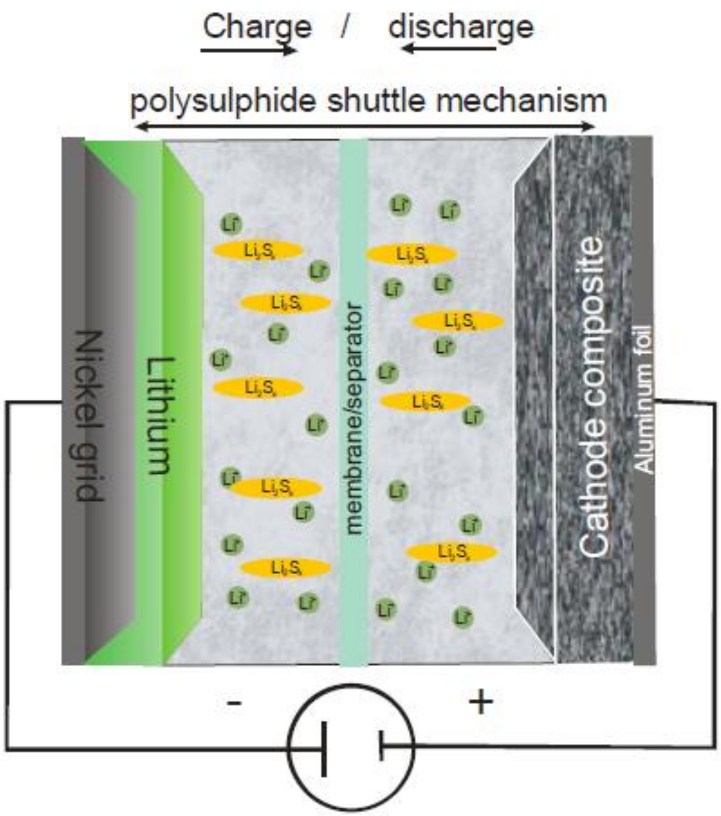
$$S_8 + Li^+ + e^- \rightarrow Li_2S_x$$

(2.4 – 2.1 V)

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

(2.1 – 1.5 V)

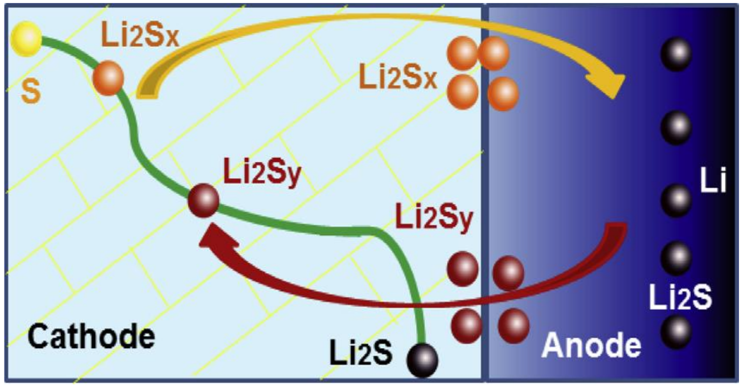
The reactions include solid-liquid-solid transformation, causing great complexity



Advantages and disadvantages

Advantages

- High energy density (2600 W h kg^{-1})
- High capacity (1642 mA h/g)
- Low cost (S is abundant)
- Environmental friendliness

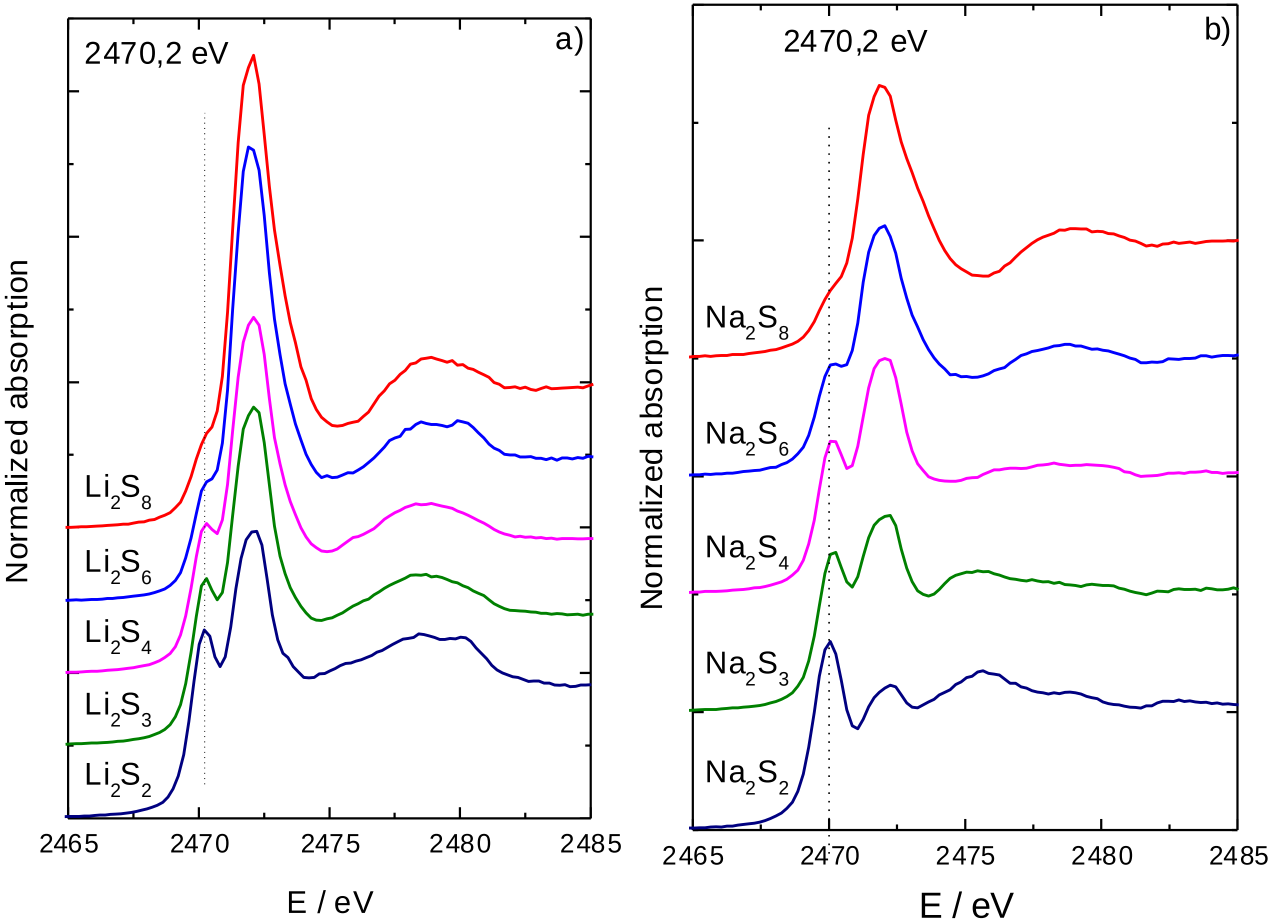


Cheng et al.,
J. Power Sour. 253, 263 (2014)

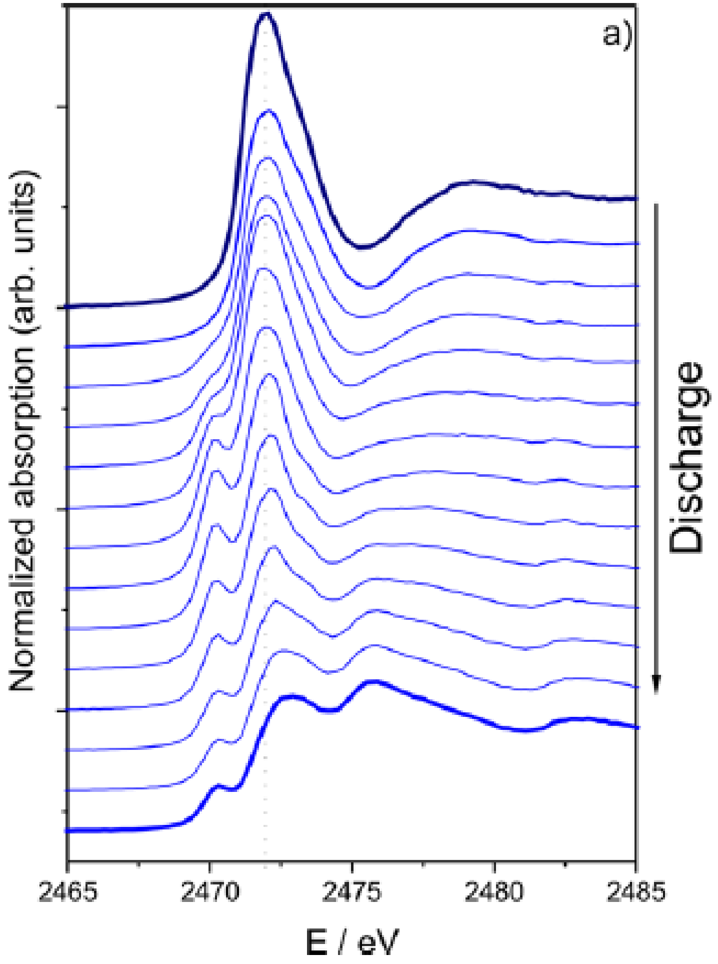
Disadvantages

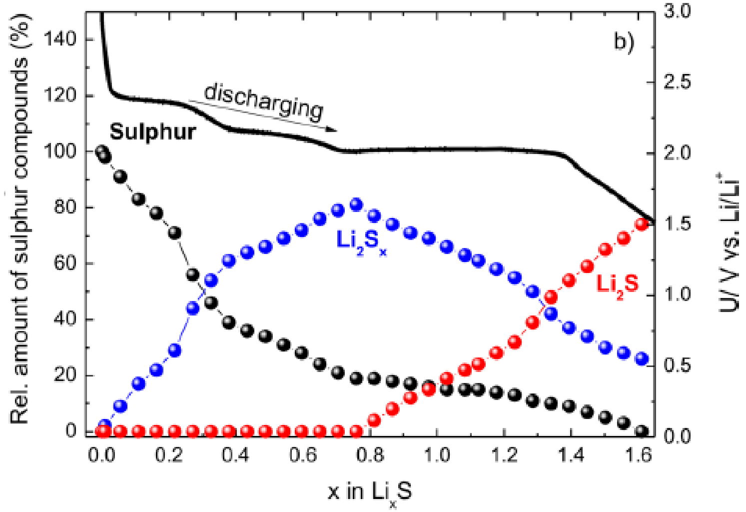
- Poor conductivity of S
- Volume variation of S (→ capacity fading)
- Polysulfide shuttle mechanism
- **Short lifetime**

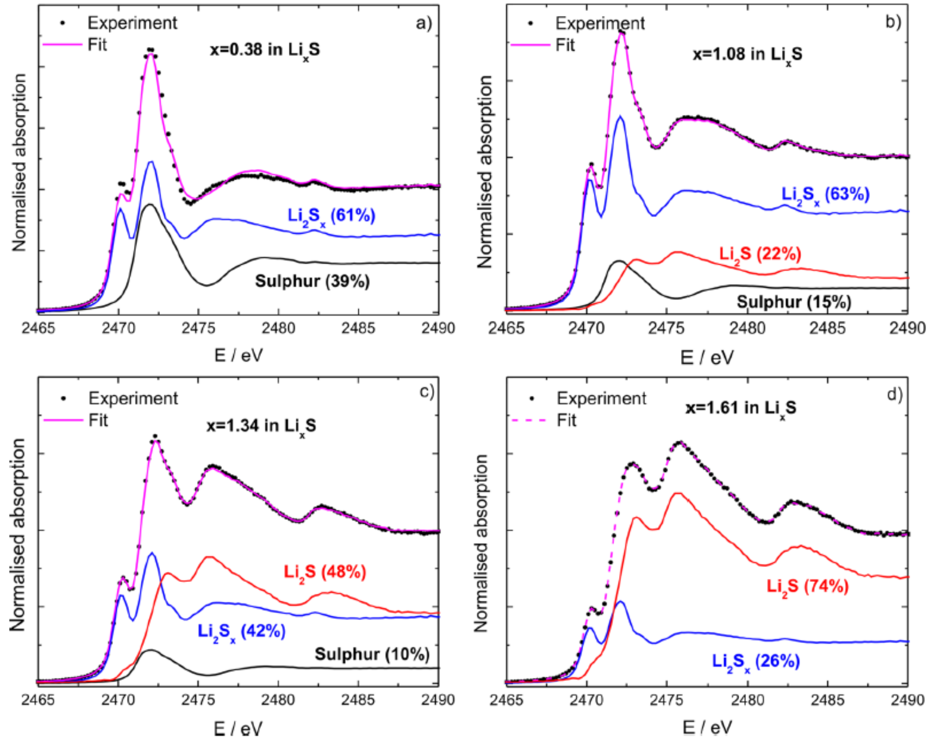
XANES of polysulphides



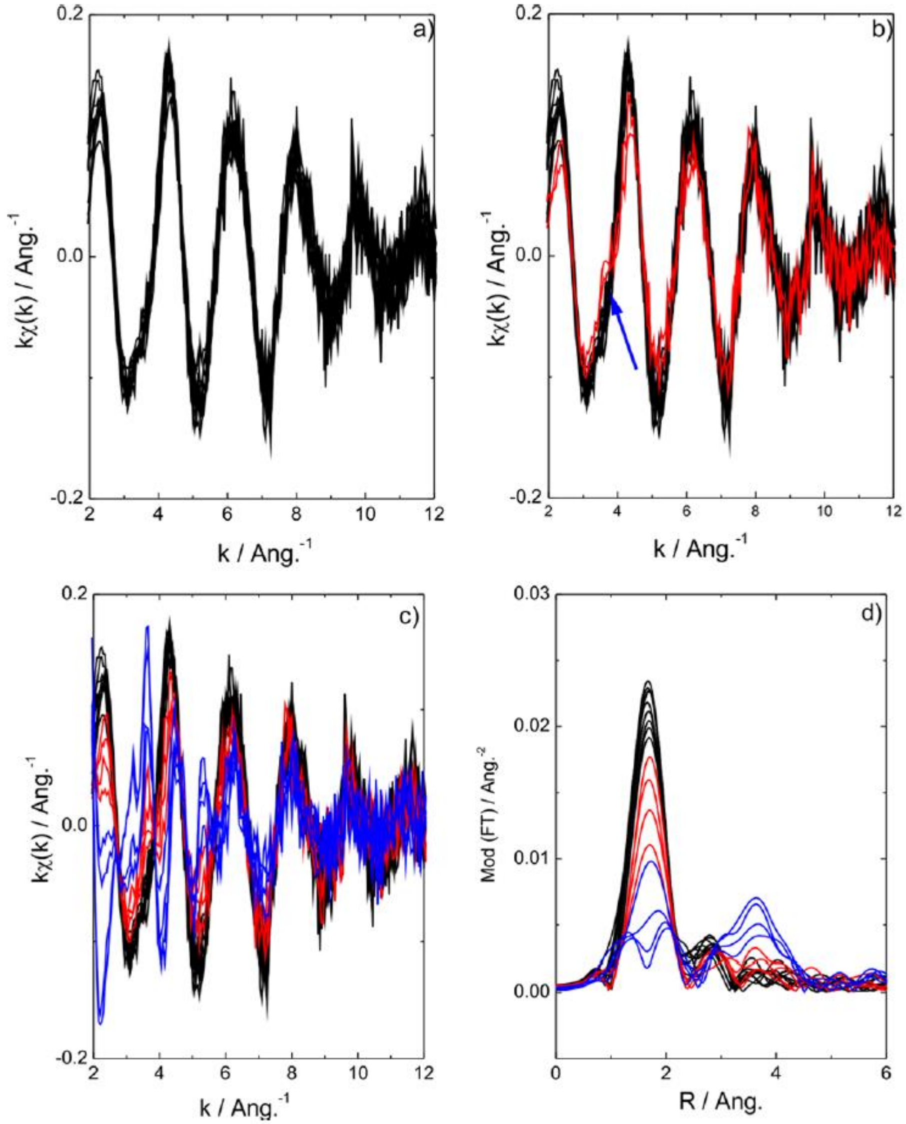
M. U. M Patel et al.,
ChemPhysChem 2014 15, 894-904


a)
Normalized absorption (arb. units)
Discharge
2465
2470
2475
2480
2485
E / eV


b)
Rel. amount of sulphur compounds (%)
140
120
100
80
60
40
20
0
discharging
Sulphur
Li_2S_x
Li_2S
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
x in Li_xS
3.0
2.5
2.0
1.5
1.0
0.5
0.0
U/ V vs. Li/Li^+


a)
Experiment
Fit
x=0.38 in Li_xS
Li_2S_x (61%)
Sulphur (39%)
Normalised absorption
2465
2470
2475
2480
2485
2490
E / eV
b)
Experiment
Fit
x=1.08 in Li_xS
Li_2S_x (63%)
Li_2S (22%)
Sulphur (15%)
Normalised absorption
2465
2470
2475
2480
2485
2490
E / eV
c)
Experiment
Fit
x=1.34 in Li_xS
Li_2S (48%)
Li_2S_x (42%)
Sulphur (10%)
Normalised absorption
2465
2470
2475
2480
2485
2490
E / eV
d)
Experiment
Fit
x=1.61 in Li_xS
Li_2S (74%)
Li_2S_x (26%)
Normalised absorption
2465
2470
2475
2480
2485
2490
E / eV

EXAFS results



High voltage plateau

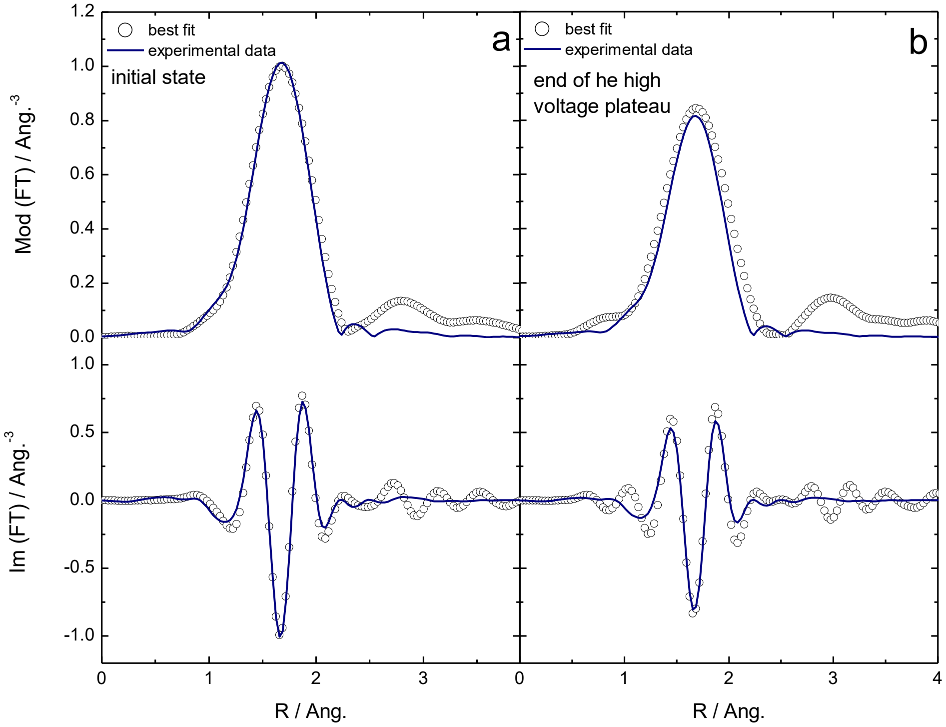
- Same main frequency
- Decrease of the intensity
- Compatible with the decrease of the average number of nearest neighbors of sulfur because of the formation of PS

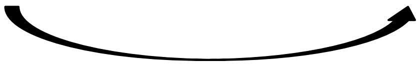
Start of the low voltage plateau

- Appearance of an extra frequency
- Attributed to the onset of the occurrence of Li_2S

R. Dominko et al.,
J. Phys. Chem. C 2015 119, 19001-19010

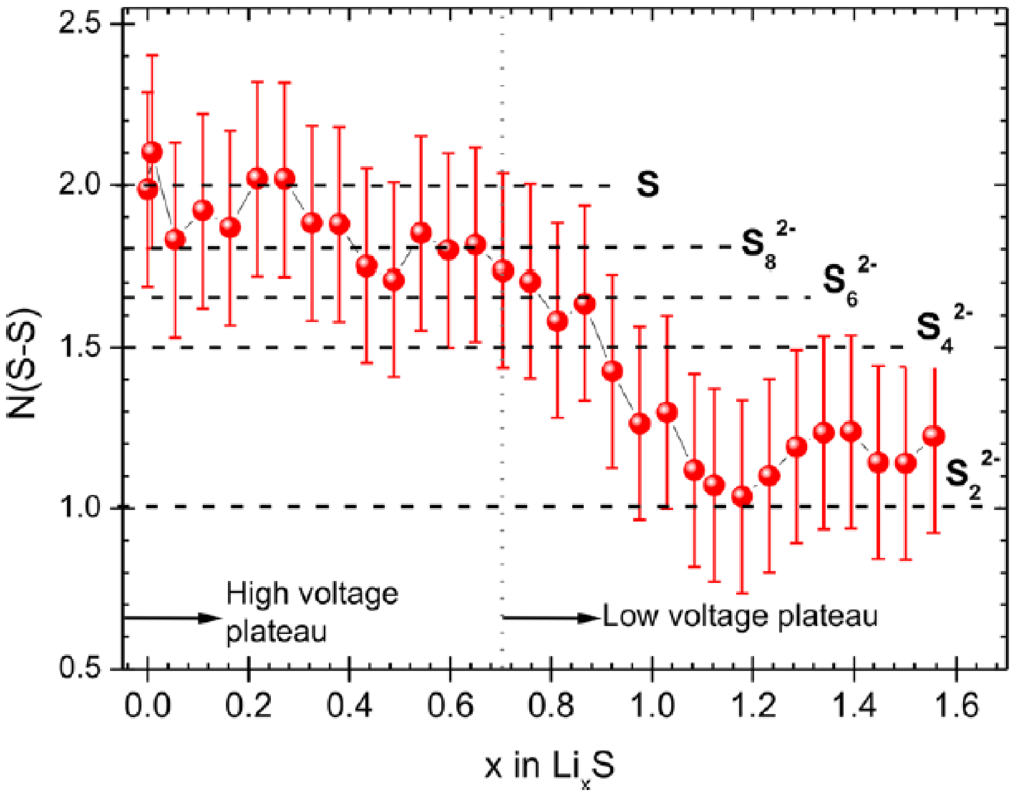
EXAFS results – quantitative analysis





N=2

N=1.6(2)

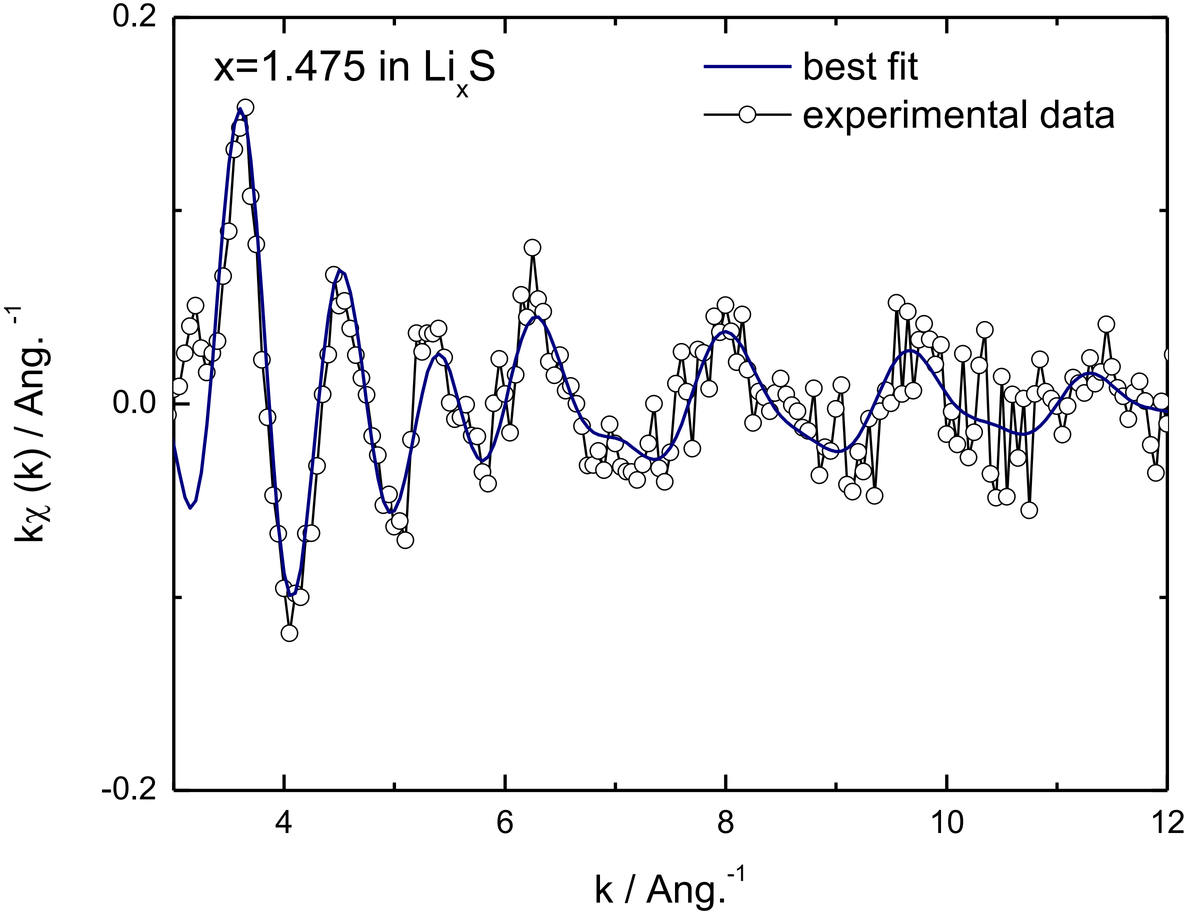


- Sharp decrease of CN at the beginning of the low voltage plateau
- CN constant at the end of the discharge

R. Dominko et al.,
J. Phys. Chem. C 2015 119, 19001-19010

Project n. 314515

EXAFS results – quantitative analysis



- S/Li_2S = 30(5)/70(5)
- No other signal ruling out any specific interaction of the S species with the composite or the electrolyte

R. Dominko et al.,
J. Phys. Chem. C 2015 119, 19001-19010

Summary

- XAS (XANES + EXAFS) in operando conditions
- The use of zeolite additive retains the polysulfides in the cathode up to a certain extent
- The use of S-free electrolyte allowed us to do a full EXAFS analysis
- The concentration of PS reached a maximum at the end of the high voltage plateau
- From the EXAFS we detect clearly the onset of the formation of Li_2S
- No other components, apart form S and Li_2S, have been detected and therefore no interaction between the cathode and the composite have been evidenced

Project n. 314515 www.eurolis.eu

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Cultural heritage

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What is Cultural heritage

- Cultural Heritage is an expression of the ways of living developed by a community and passed on from generation to generation, including customs, practices, places, objects, artistic expressions and values. Cultural Heritage is often expressed as either Intangible or Tangible Cultural Heritage (ICOMOS, 2002).
- As part of human activity Cultural Heritage produces tangible representations of the value systems, beliefs, traditions and lifestyles. As an essential part of culture as a whole, Cultural Heritage, contains these visible and tangible traces from antiquity to the recent past.
- Driving force behind all definitions of Cultural Heritage is:

  it is a human creation intended to inform (John Feather, 2006).

Introduction

- Scientific investigations on tangible cultural heritage are in general based on a strong interdisciplinary approach, which implies the collaboration among scientists and archaeologists expert in many different fields
- Knowledge exchange among research groups is required by the number of different conventional and advanced techniques which can be applied to ancient materials.
- One of the main requirements imposed by the archaeologists in the studies of ancient and precious materials is that the selected techniques must be non-destructive (or at most micro-destructive).
- A peculiar characteristic of the archaeological finds is that they are often heterogeneous (organic/inorganic, crystalline/amorphous) and complex in shape and composition (pottery, glass, metals, paper, pigments, wood, cloths, etc.) and are often covered by alteration layers

Introduction

The questions that archaeologists ask more often regarding an ancient object are:

- what material is it made of (composition)?
- when was it made (dating)?
- where was it made (provenance)?
- how was it made (art technology)?
- how can we avoid its destruction (conservation)?

Introduction

- Synchrotron radiation-based methods can play a central role, being specifically suitable for micro-non-destructive analyses
- Using synchrotron radiation, experiments based on very brilliant and collimated micro-beams of X-rays are employed to obtain diffraction, spectroscopic and imaging data with unprecedented space and energy resolution

SR techniques for CH

- Elemental microanalysis down to the sub-ppm level by means of X-ray fluorescence analysis (µ-XRF).
- Local chemical state determinations of selected (trace) constituents using XAS and µ-XAS (X-ray absorption spectroscopy)
- Information on the presence and nature of crystalline phases via X-ray diffraction (XRD), which usually employs X-ray photons with energies in the 0.5–30 keV range.
- Imaging of entire objects using high energy SR to allow high quality radiographic or tomographic measurements, revealing the internal structure of these artifacts

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XAS applied to CH

- Non-invasive
- It can be applied in air
- Low detection limit
- High lateral resolution
- Chemical sensitivity
- It does not require any restriction on the type and size of the sample (metal, ceramic, glass, cloth, paper, etc.)
- It is applicable to most of the elements of interest
- Straightforward access to oxidation states and more generally to chemical speciation

Which information from XAS for CH

- Chemistry involved in both the object's history (Choice of ingredients, manufacturing processes such as extraction of materials , purification heat treatment and chemical synthesis, geographic provenance, trade routes) and future (during preservation and restoration treatments)
- Explanation of optical effects occurring in historical glasses or ceramics by probing the molecular environment of relevant chromophores
- Insights into craft skills that were mastered years, decades, or centuries ago but were lost over the course of time
- Characterization of unwanted reactions, alteration phenomena that can dramatically alter the object's original visual properties (while the elemental composition is unchanged)

XAS applied to historical glasses

- Historical vitreous materials were highly appreciated because of their optical properties.
- Interplay between transparency, opacity, color, metallic shine, colored iridescence.
- Such effects can be induced by the presence of opacifying crystals, ionic chromophores, metallic nanoparticles
- The oxidation state of elements and more generally their chemical environment within the vitreous matrix is directly correlated to these optical effects.
- The historical production method therefore required adequate control of firing conditions (temperature, atmosphere, and time), as well as the introduction of oxidizing or reducing ingredients

Coloring variations are usually obtained in glass by modulating the oxidation states of transition elements such as Mn, Fe, Co, and Cu; these elements have characteristic absorption frequencies in the visible region as a result of d-d electronic transitions

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

- Study of ancient glasses from Patti Roman Villa (Messina, Sicily)
- From the chemical point of view, the samples are 'low-magnesia' glasses, with a composition typical of the Roman period
- Glasses of different colors from light green to pale brown
- Fe and Mn K-edge XANES

Aim of the work

- To test the influence of iron oxidation state on the color of the studied samples
- To identify the possible decolorant role of manganese oxide in the almost uncolored samples

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

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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

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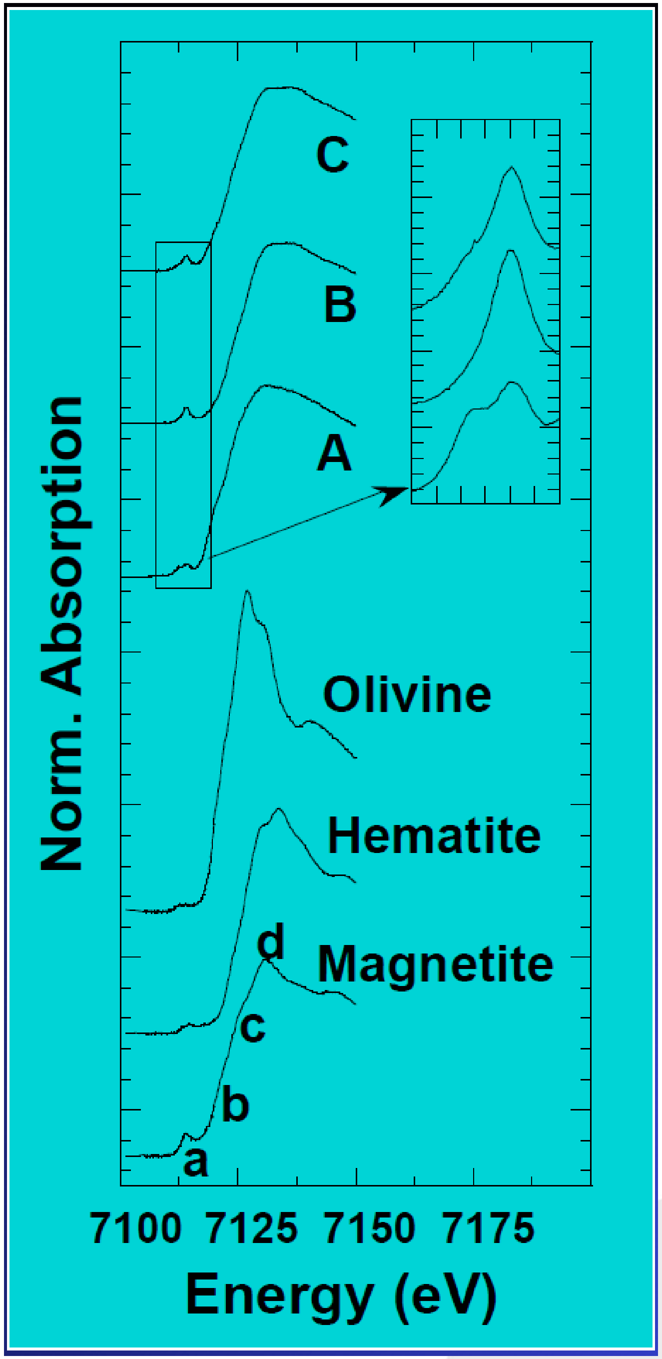
Fe and Mn K-edge XANES study of ancient Roman glasses

Glass A: pale green

Glass B: uncolored

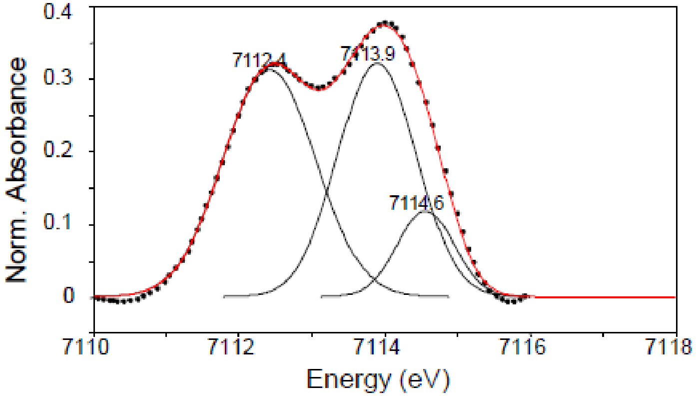
Glass C: pale brown



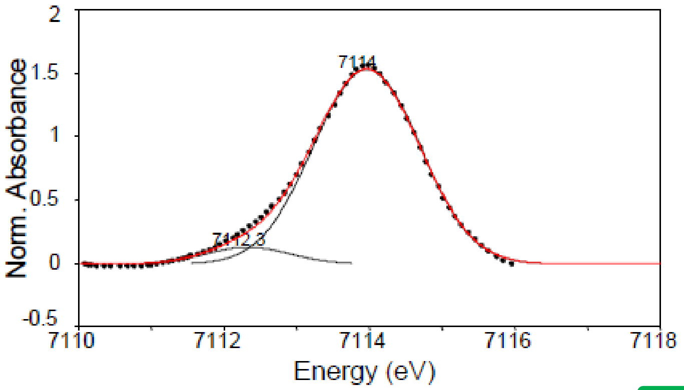
- B and C similar to each other: both in the general Shape and in the energy position of the different features
- Features (b) and (d) fall at high energy characteristic of Fe^{3+}

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

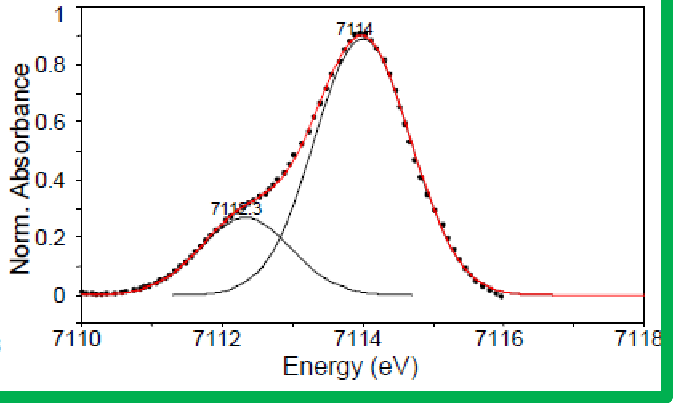
Fe and Mn K-edge XANES study of ancient Roman glasses



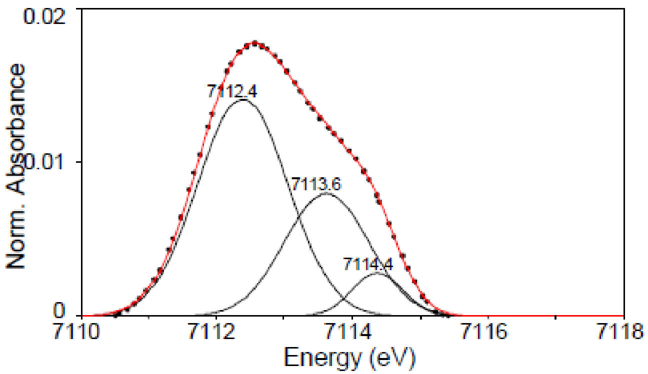
Glass A



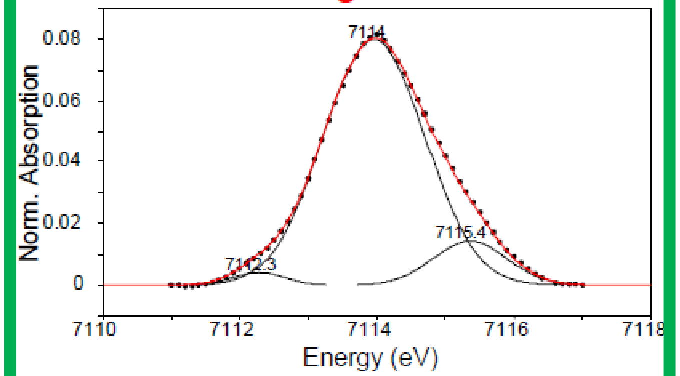
Glass B



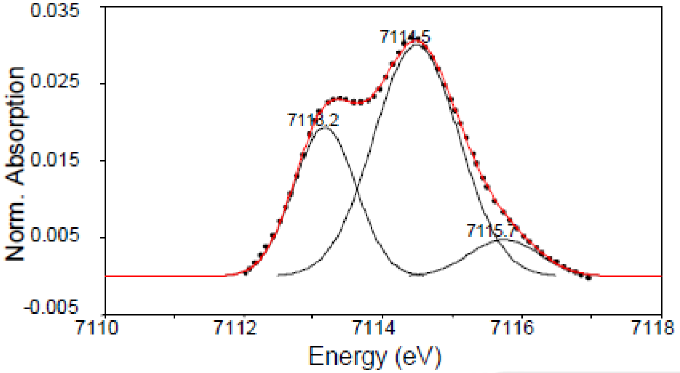
Glass C



Olivine



Magnetite



Hematite

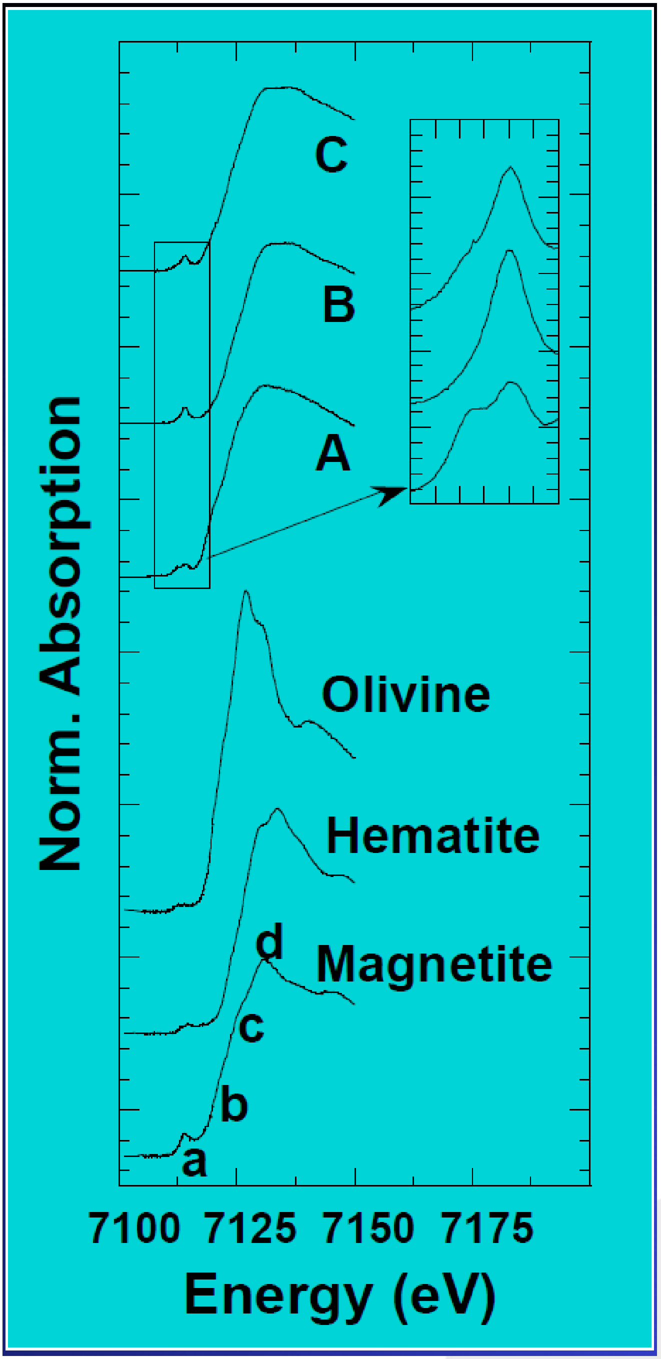
S. Quartieri et al., Eur. J. Min. (2002) 14(4),749-756

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

Glass A: pale green

Glass B: uncolored

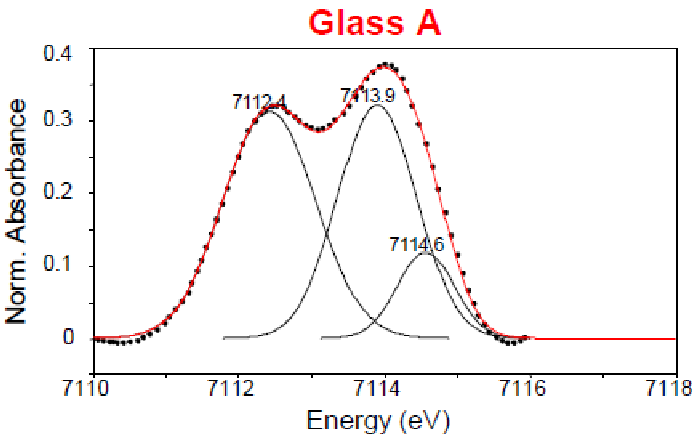
Glass C: pale brown

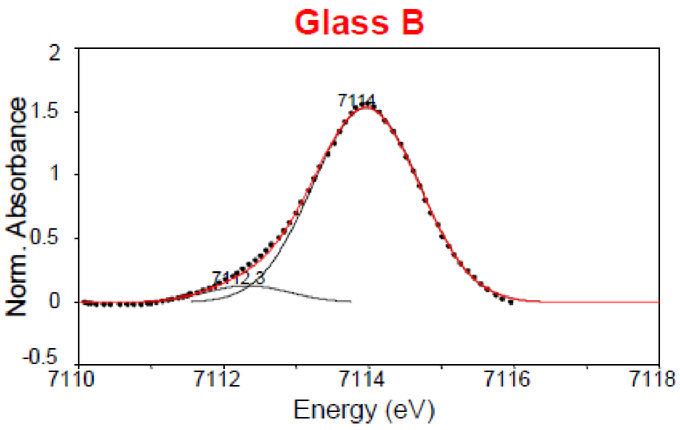


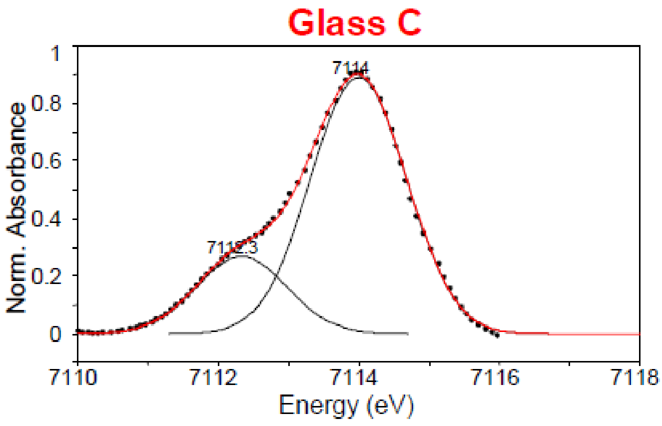
- In sample A the features (b) and (d) are at much lower energy, nearer to those present in the olivine spectrum characteristic of Fe^{+2}

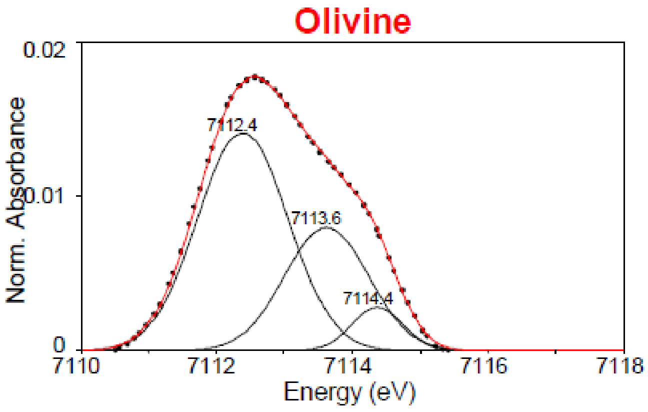
S. Quartieri et al., Eur. J. Min. (2002) 14(4),749-756

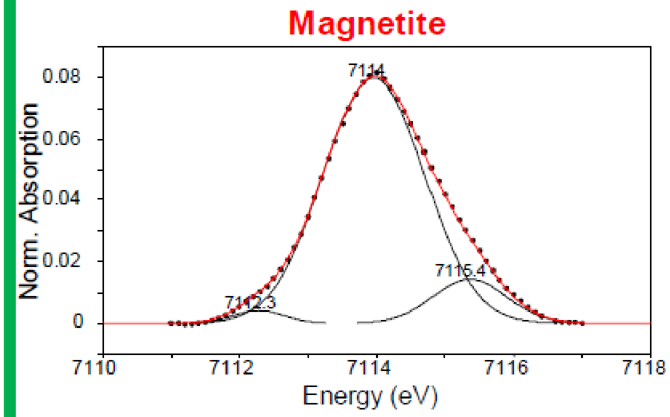
Fe and Mn K-edge XANES study of ancient Roman glasses

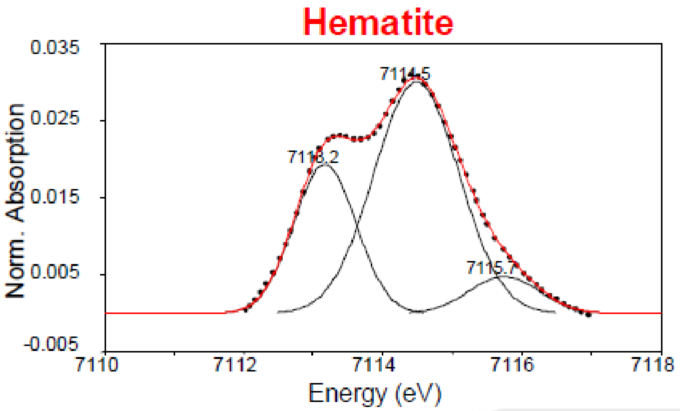












S. Quartieri et al., Eur. J. Min. (2002) 14(4),749-756

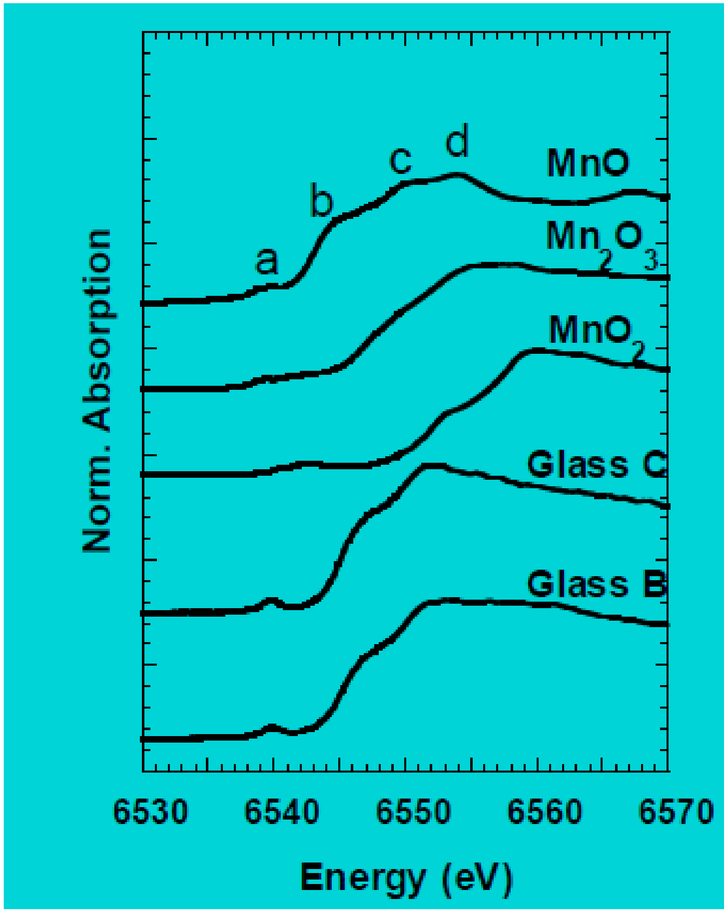
Fe and Mn K-edge XANES study of ancient Roman glasses

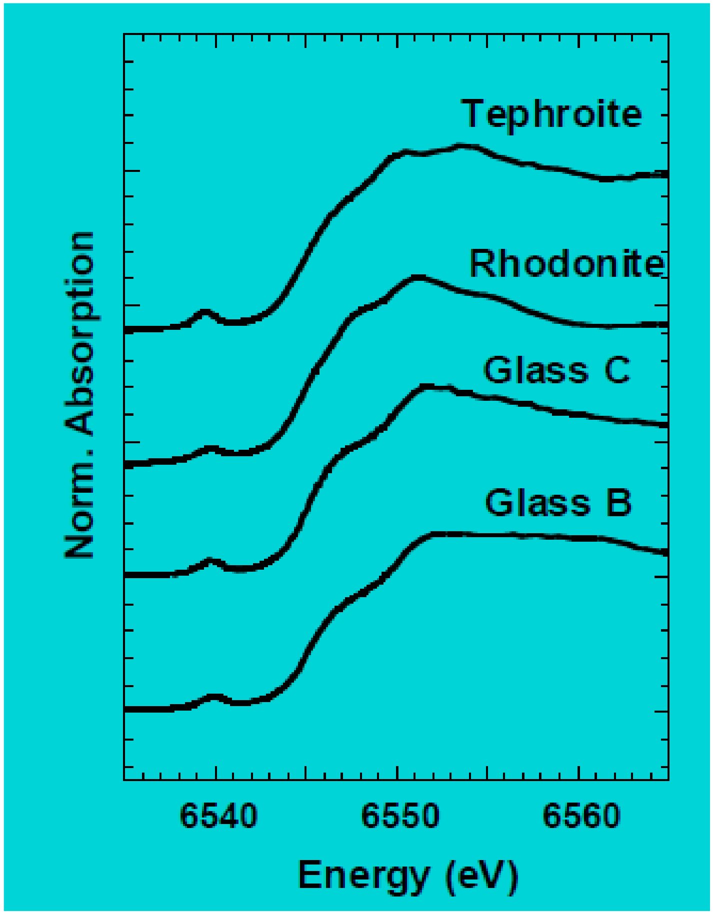
Glass A: pale green
Glass B: uncolored
Glass C: pale brown

- In glass C and in glass B, Fe is predominantly in 3+ oxidation state
- In glass A there is a high percentage of Fe^{2+}

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

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





- Mn is in reduced form
- Strong similarity between the two Mn^{2+}-silicatic reference compounds

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

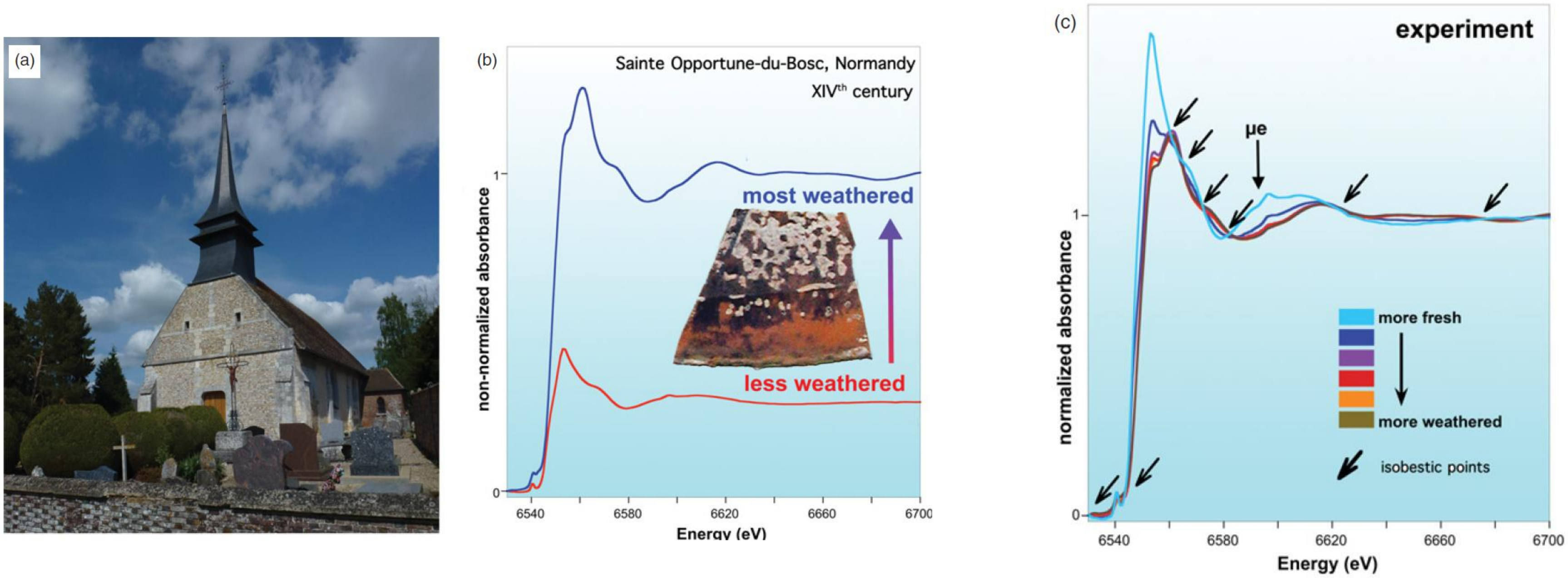
Glass A: pale green
Glass B: uncolored
Glass C: pale brown

Conclusion

- In sample B and C, Mn^{4+} has oxidised Fe^{2+} to Fe^{3+} and therefore is present in the reduced form
- It is confirmed the hypothesis of a redox interaction between manganese and iron as a results of a deliberate addition of pyrolusite (mineral containing MnO_2) – reported in literature as the main decolorant in the Roman period – during the melting procedure of the uncolored glass

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

XAS study on glasses



- The oxidation of Mn^{2+} into Mn^{4+} has been observed in medieval glass windows exposed to progressive weathering in Cathedral du Bosc, Normandy, France.
- This oxidation results in the precipitation of manganese oxi-hydroxides, which in turn lead to opacification and a change in color (brown) of the glass panes.

F. Farges et al., Phys. Scr.. (2005) T115,885-887

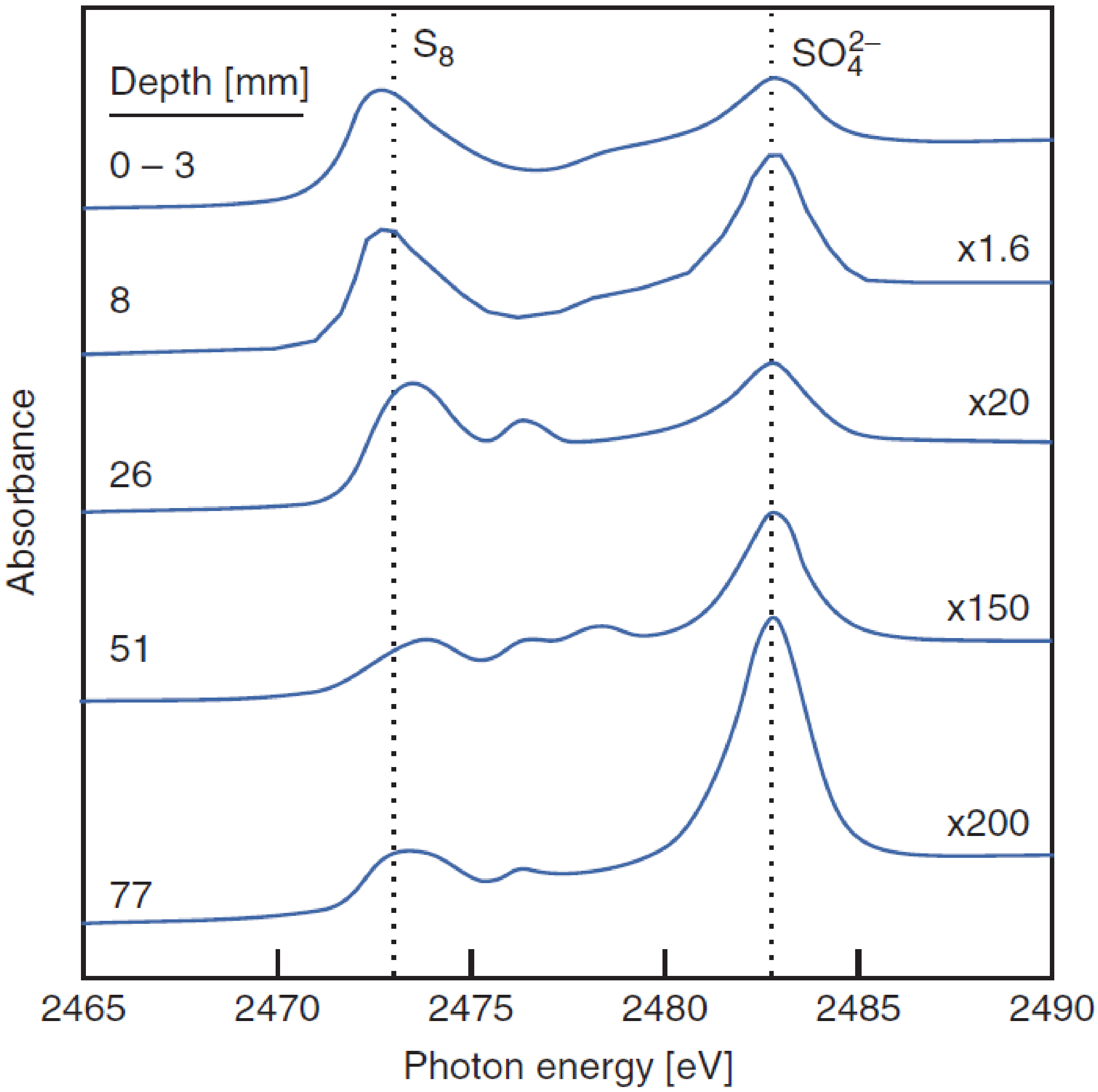
Preservation of the XVII-century Warship VASA - 1

M. Sandstrom et al., *Nature*, 415, pp. 893–897, 2002.

- It sunk to a depth of 30 m in Stokholm harbour in 1628
- The salty and anaerobic conditions of the harbours water prevented wood-consuming plants, fauna or bacteria, from attacking the ship, thereby preserving the VASA in excellent conditions.
- It was raised in 1961 and after 30 years of preservation treatment was put on display in Stockholm in 1990.
- First problems detected in 2000
  - Crusty patches of salt in the surface
  - Softening of the woods

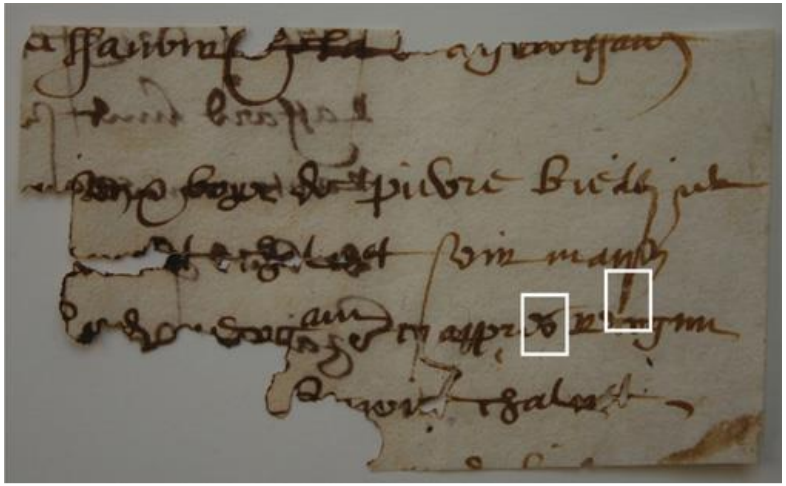
Preservation of the XVII-century Warship VASA - 2

- Combined XPS, XRD and XANES have revealed the presence of elemental sulfur nearly everywhere within the timbers, ready to be oxidized
- Large amounts of sulfates and sulfuric acid were also detected, suggesting that the oxidation has spread to many parts of the vessel, critically endangering its structure
- XANES had to be used instead of XRD because of the poor crystallinity of the sample and because of the spurious signals originating from the wood.
- XANES analyses have also shown the presence of intermediate redox states of S, suggesting a continuous oxidation throughout the ship.



XANES analysis of Fe valence in iron gall inks

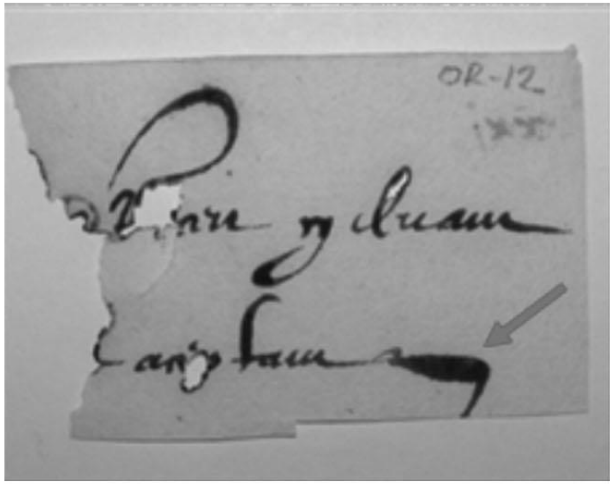
- Iron gall inks (Fe(II)-sulfate + gallic acid) is one of the most important inks in the history of the western civilization, of a widespread use from the middle ages until the 20th century
- These inks induce degradation of paper
- The two main reasons for iron gall ink corrosion are:
    - hydrolysis of cellulose because of acidity of the ink
    - Oxidative decomposition of cellulose catalyzed by ferrous ions
- Determination of the concentration of Fe^{2+} in inks in historic documents is therefore relevant in assessing the potential risk of further oxidation of cellulose and in devising an effective stabilization treatment



I. Arcon et al., *X-ray Spectrometry*, 36, pp. 199–205, 2007.

XANES analysis of Fe valence in iron gall inks

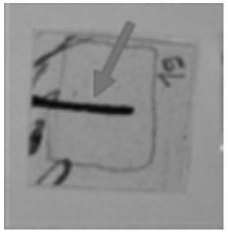
OR-1



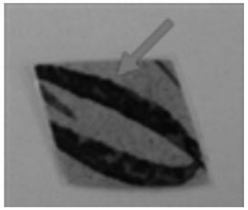
OR-2

OR-4

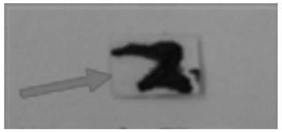
OR-3



OR-6



OR-5



- XANES has been used to determine Fe^{2+}/Fe^{3+}
- Model compounds of iron gall ink have been prepared with different amount of Fe^{2+}/Fe^{3+}
- Standard compounds with well established Fe valence and local symmetry were also measured

I. Arcon et al., *X-ray Spectrometry*, 36, pp. 199–205, 2007.

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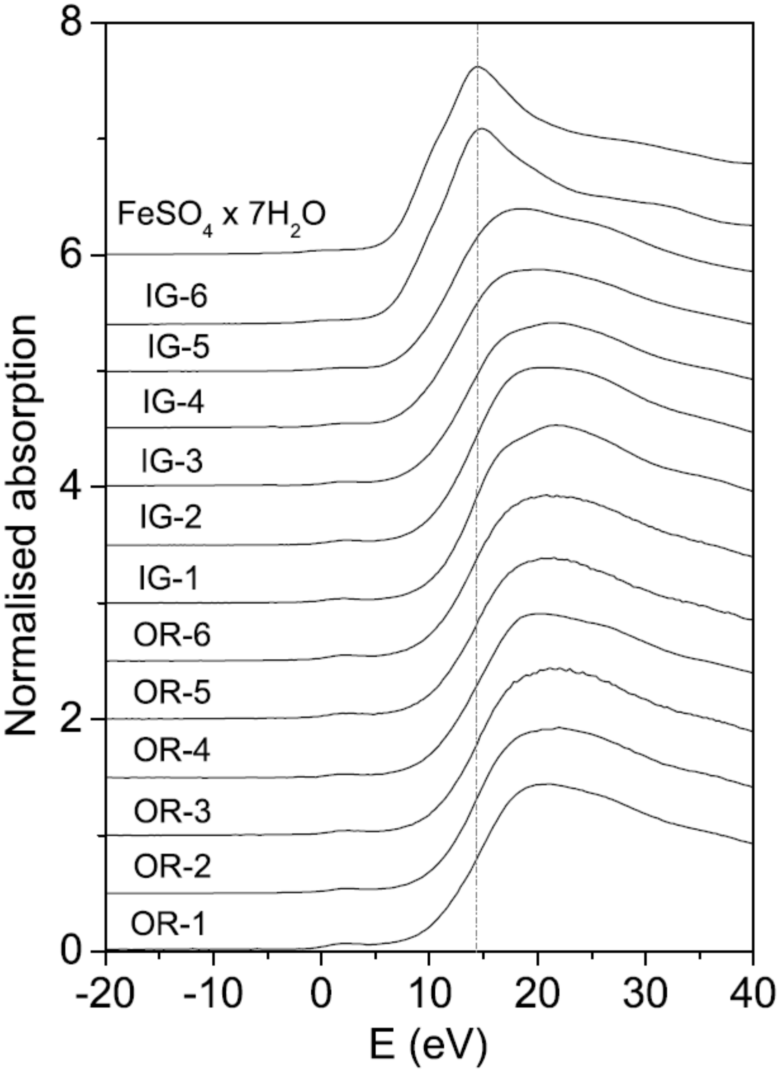
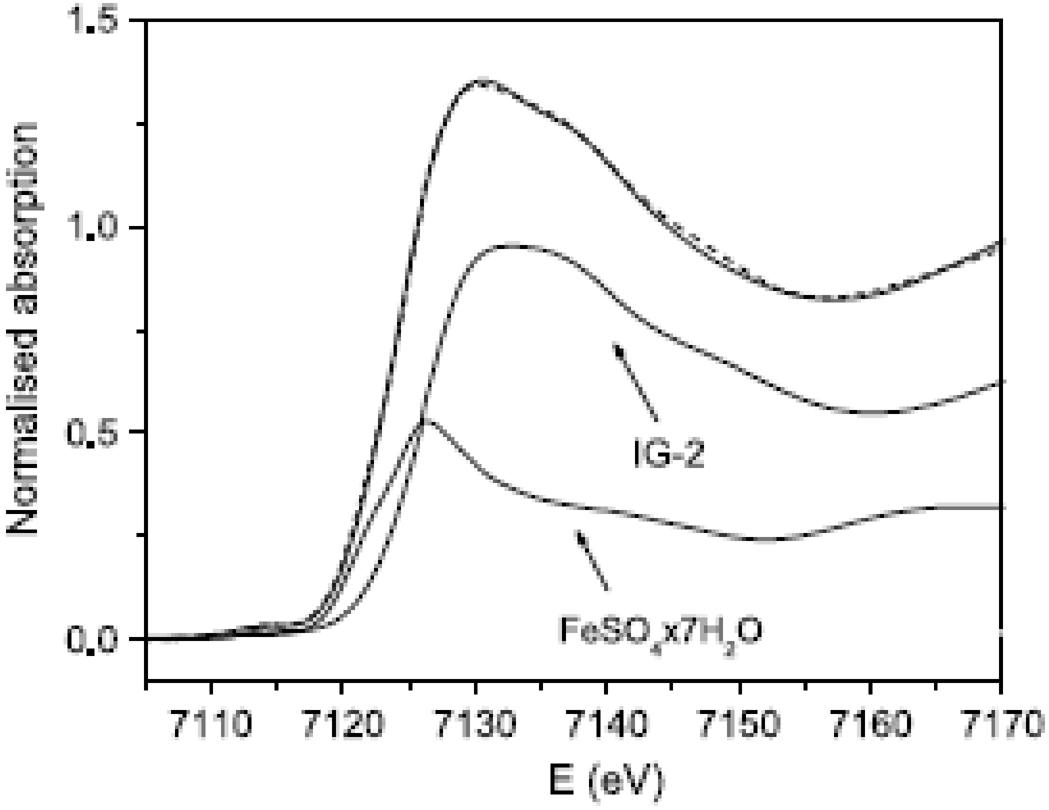
XANES analysis of Fe valence in iron gall inks





I. Arcon et al., *X-ray Spectrometry*, 36, pp. 199–205, 2007.