A practical approach to XANES data analysis

*How to understand **local atomic structure, coordination chemistry** and **electronic state** from XANES spectra*

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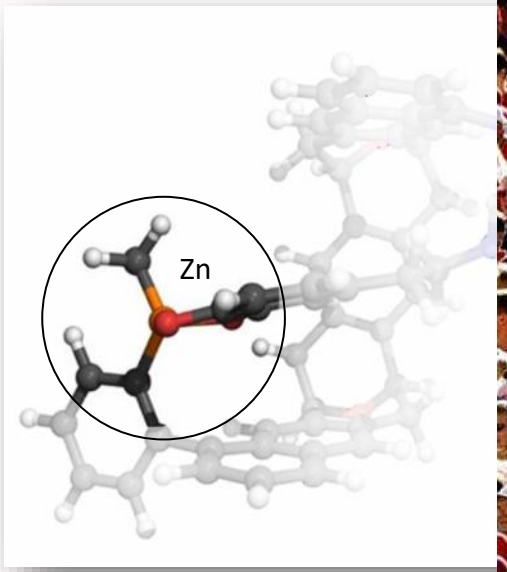
XVIII Gilberto Vlaic School on Synchrotron Radiation
Fundamentals, Methods and Applications
Muggia, Italy · 21 September - 1 October 2026

XAFS: an *element-selective* probe of *local structure*

Local atomic structure from the absorber's point of view

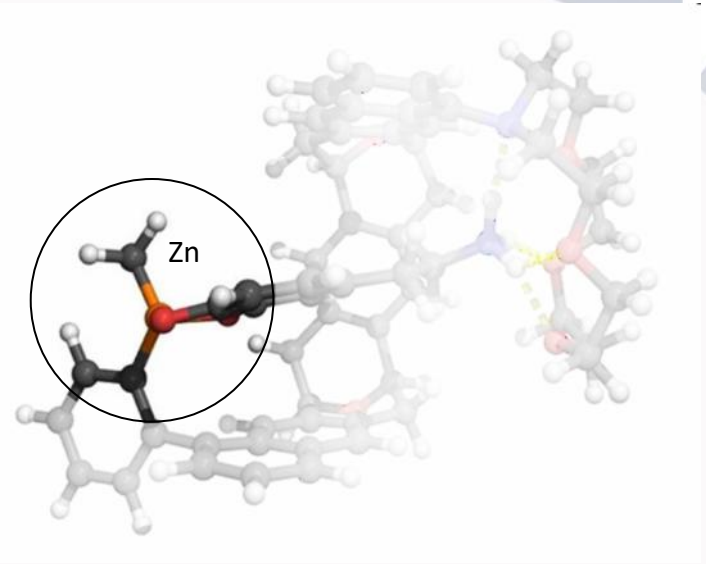


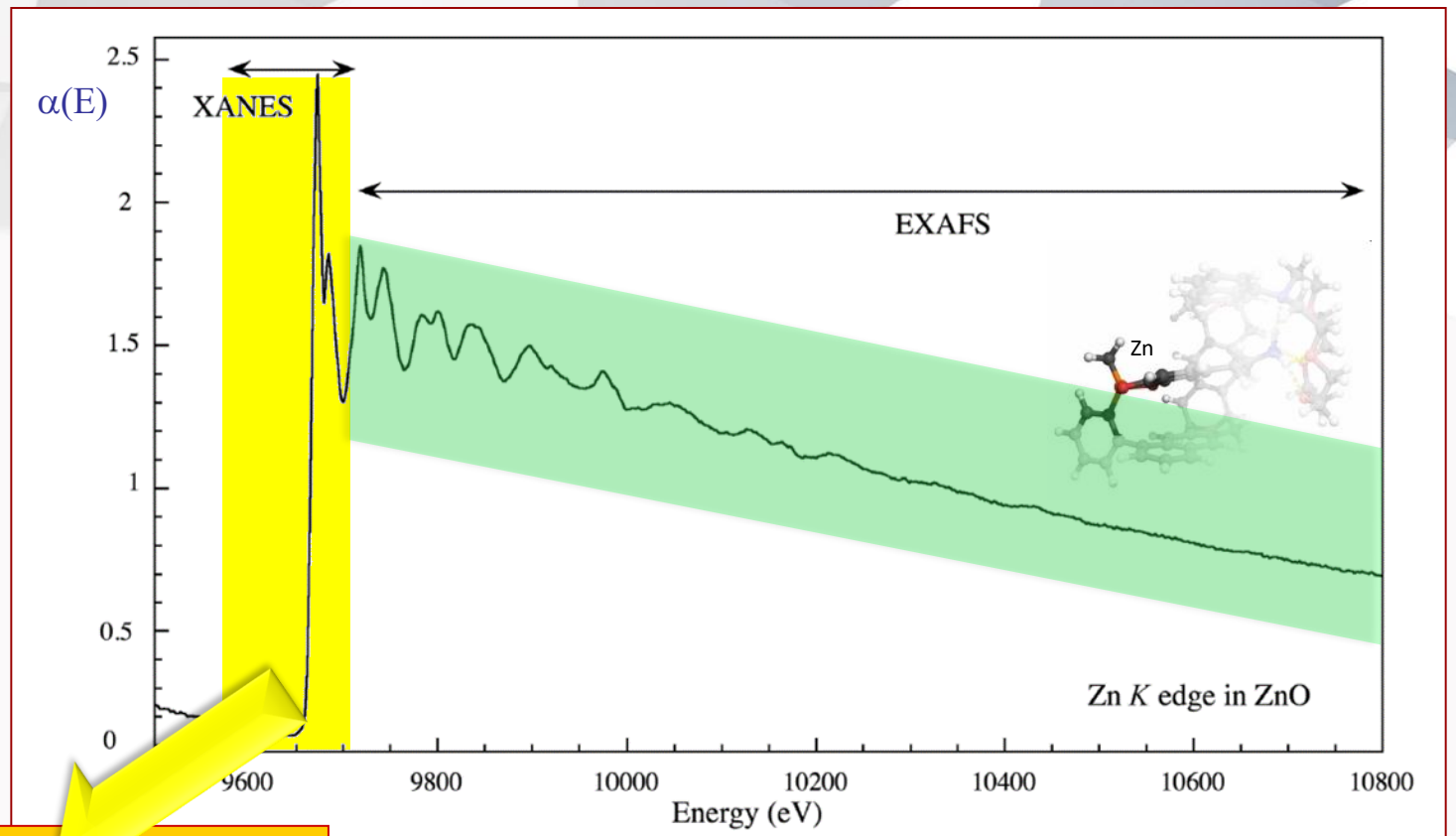
What XAFS measures

can provide average **structural**, **electronic** and even **magnetic** information about absorbers

Key features of XAFS

- Applicable to materials in **any physical state**: gases, liquids, solids, single crystals, powders, amorphous materials, nanostructures, etc.
- Applicable from **bulk materials to highly diluted systems** (µM–nM range)
- **Highly versatile**: bulk materials, surfaces, layered systems, quantum structures, etc.
- (*Relatively*) **simple experimental setup** and straightforward data collection
- **Fast** (few seconds) to **ultrafast** (p-seconds) data acquisition
- **Directional sensitivity** (polarized XAS): probing structural anisotropy
- **Element-selective sensitivity to magnetic properties** (**XMCD**)

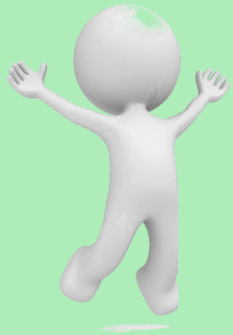




Challenges in XANES analysis:

- **Lack** of a simple analytical expression
- **Computationally demanding** theoretical calculations
- Requires **advanced theoretical expertise**

EXAFS: quantitative structural refinement



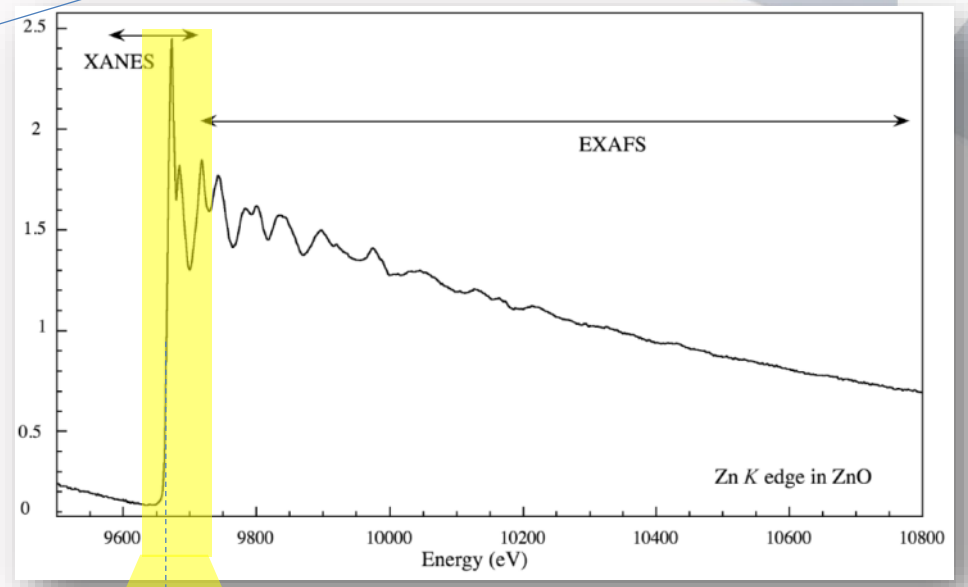
$$\chi(k) = \frac{1}{k}\sum_j A_j(k,R_j)\sin\left(2kR_j + \phi_j(k)\right)$$

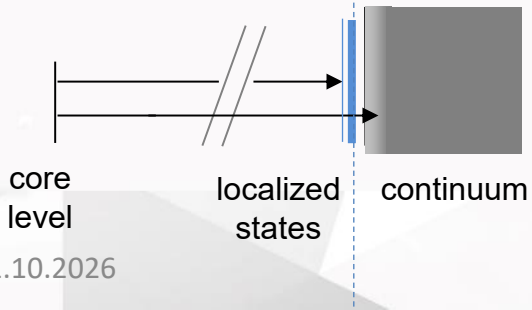
$$A_j(k,R_j) = \frac{S_o^2 N_j}{R_j^2}\left|f_j(k,R_j)\right| e^{-2k^2\sigma_j^2} e^{-\frac{2R_j}{\lambda}}$$

Why use XANES?

$$A_j(k,R_j) = \frac{S_o^2 N_j}{R_j^2} |f_j(k,R_j)| e^{-2k^2\sigma_j^2} e^{-\frac{2R_j}{\lambda}}$$

- **Stronger spectral features** and typically **higher** signal-to-noise ratio
- **Less affected by structural disorder**
- Requires a **limited energy range**
- **Simpler and faster data collection**
- Sensitive to:
  - **Electronic structure** (unoccupied density of states DoS)
  - **Local coordination geometry and symmetry**





XANES vs EXFAS: information and practical opportunities

Strong spectral features:

- **Less demanding in terms of data statistics**, sample quality, and beam intensity
- Can be measured on **more dilute samples**
- Requires **shorter acquisition times**, enabling **time-resolved experiments**

Damping of XANES signal due to structural disorder is weak:

- Matter under extreme conditions: high temperature, pressure, magnetic fields...

Electronic structure (DOS) and local symmetry:

- XANES features are particularly sensitive to the **oxidation state, coordination geometry, and local symmetry** of the absorber.
- XANES can be used as a **fingerprint for chemical speciation** in mixtures and heterogeneous systems

Restricted energy range around the absorption edge:

- Enables measurements at low photon energies (Si, S, Cl, ...)
- Allows faster data acquisition
  - ideal for time-resolved XAS
  - suited for microprobes and mapping (sub-micrometer resolution).

Element-selective magnetic information

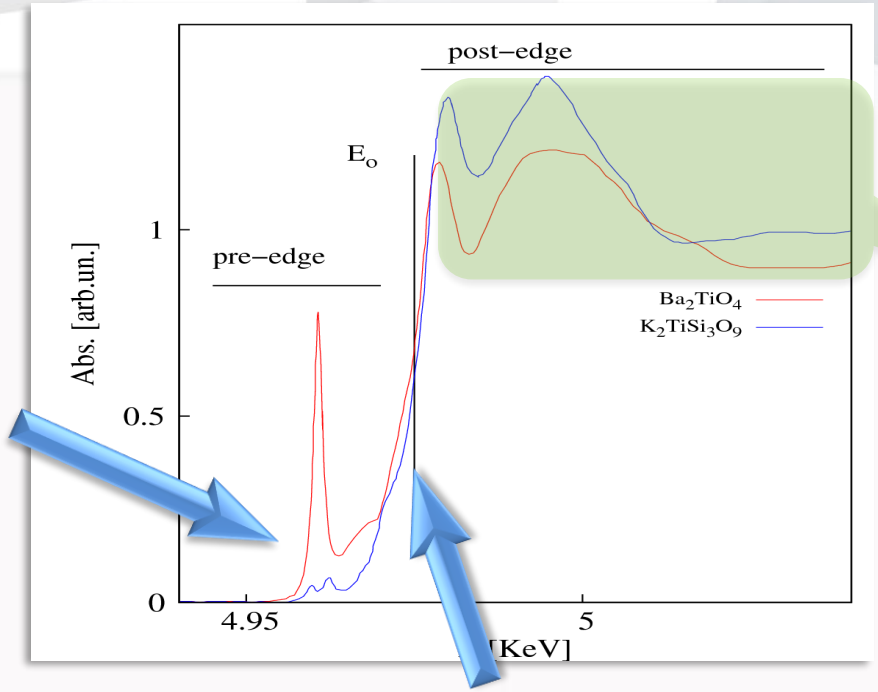
- **XMCD** provides an element-specific probe of magnetism
- Sum rules at the $L_{2,3}$ edges separate the orbital and spin magnetic moments

XANES theory is complex

- **Lack** of a simple analytical expression
- **Computationally demanding** calculations
- Requires **advanced theoretical expertise**

XANES signal is prone to *(relatively)* simple interpretation for *(relatively)* easy and fast (semi-)quantitative analysis

Pre-edge, edge and post-edge regions



Pre-edge

Features arising from electronic transitions to **localized unoccupied states** near the Fermi level.

Sensitive to the **electronic state** and **local symmetry** and **coordination geometry** around the absorber

Post-edge (XANES)

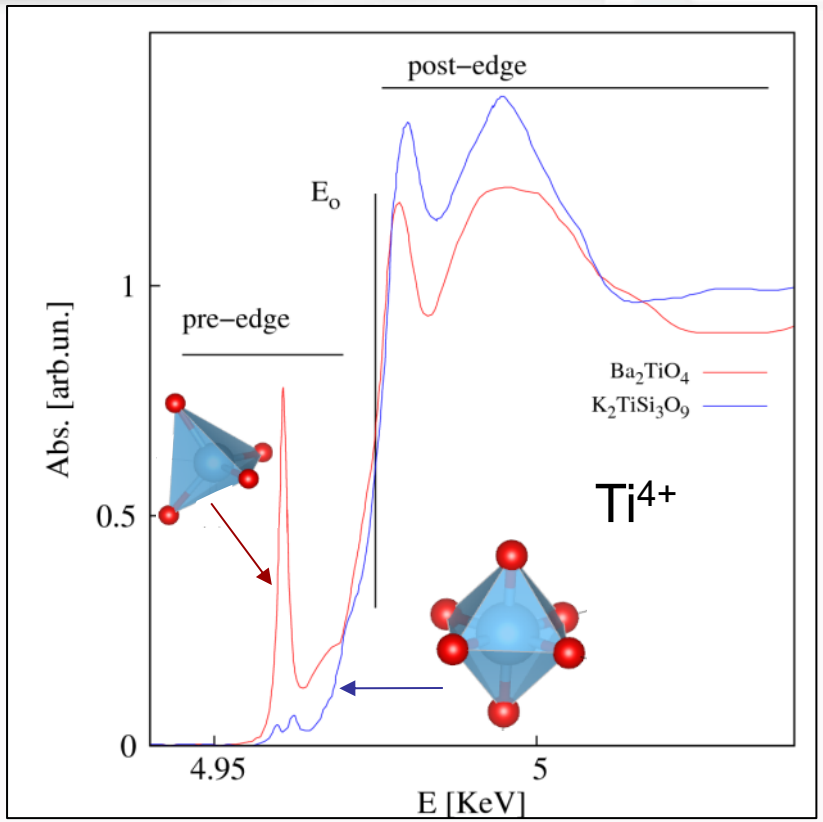
full multiple scattering (FMS)

Edge (E_0)

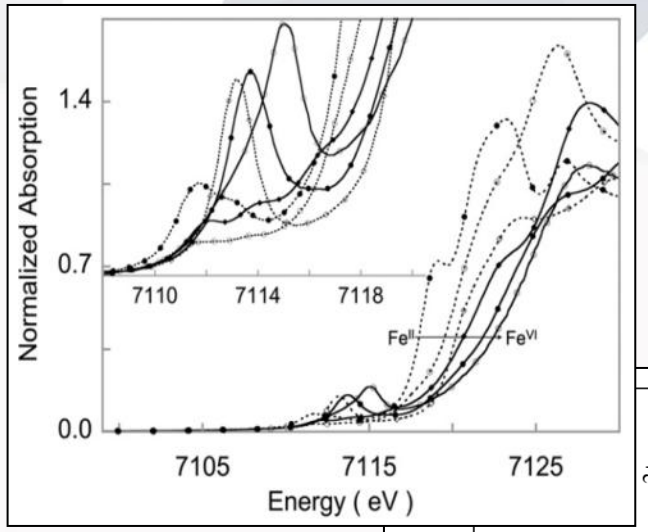
- marks the **onset of** transitions to **continuum states**
- depends on the oxidation state of the absorber
- It shifts to higher energy with increasing oxidation state, roughly by eV per oxidation unit

Oxidation state and coordination leave distinct signatures

XANES signal is prone to *(relatively)* simple interpretation for *(relatively)* easy and fast (semi-)quantitative analysis

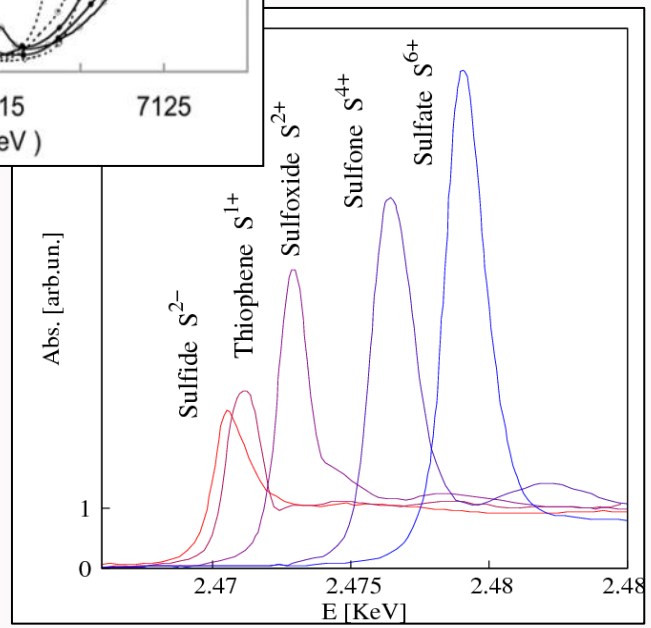


Local symmetry and XANES in Ti^{4+} compounds



Fe K edge: coordination complexes

R. Sarangi, Coord. Chem. Rev. **257** 459–472 (2013)



Sulfur K edge: chemical shifts across oxidation states

XANES features reflect the (average) local coordination environment:

coordination number, ligand type, and local symmetry

Edge position is sensitive to the absorber's **oxidation state.**

Early years of XANES

The Pre-edge region of **argon**

Below the ionization threshold, excitation to bound states produces **discrete resonances**.

Each transition has a **characteristic line shape / intensity** determined by the **core-hole lifetime** (Lorentzian broadening), convoluted with the experimental **energy resolution** (Gaussian broadening).

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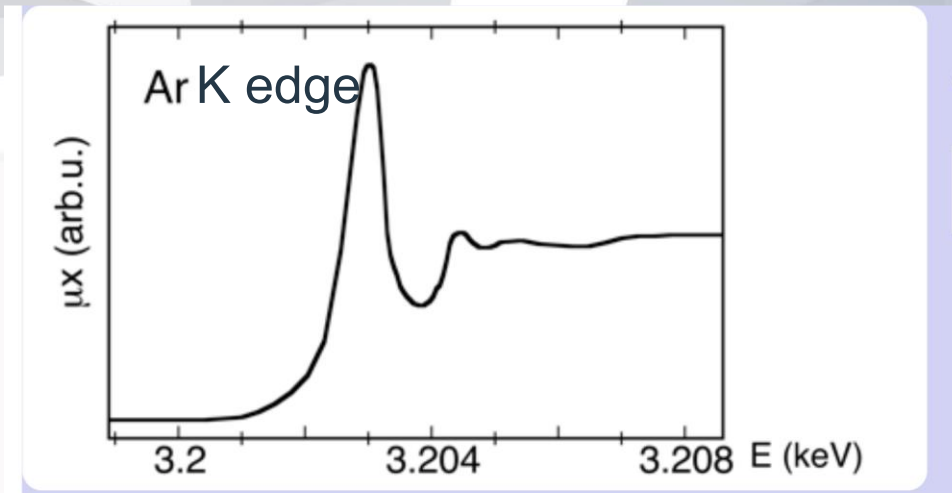
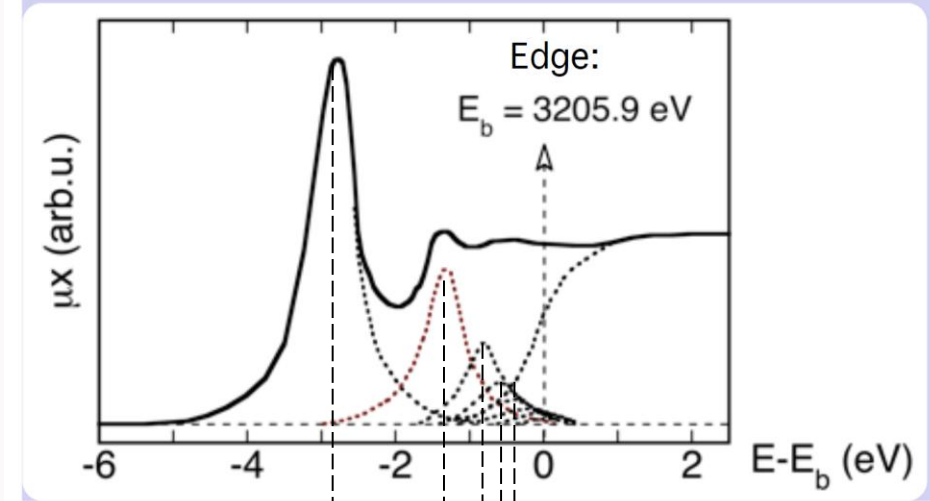


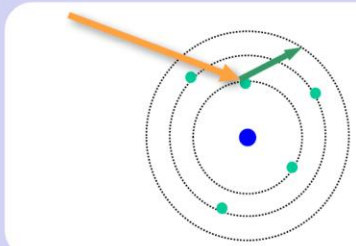
Experiment

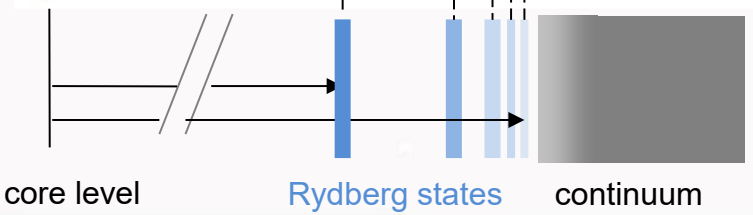
L. G. Parratt,
Phys. Rev. 56, 295 (1939)

Energy resolution ~ 0.6 eV



Interpretation:
- Rydberg levels
- edge to continuum



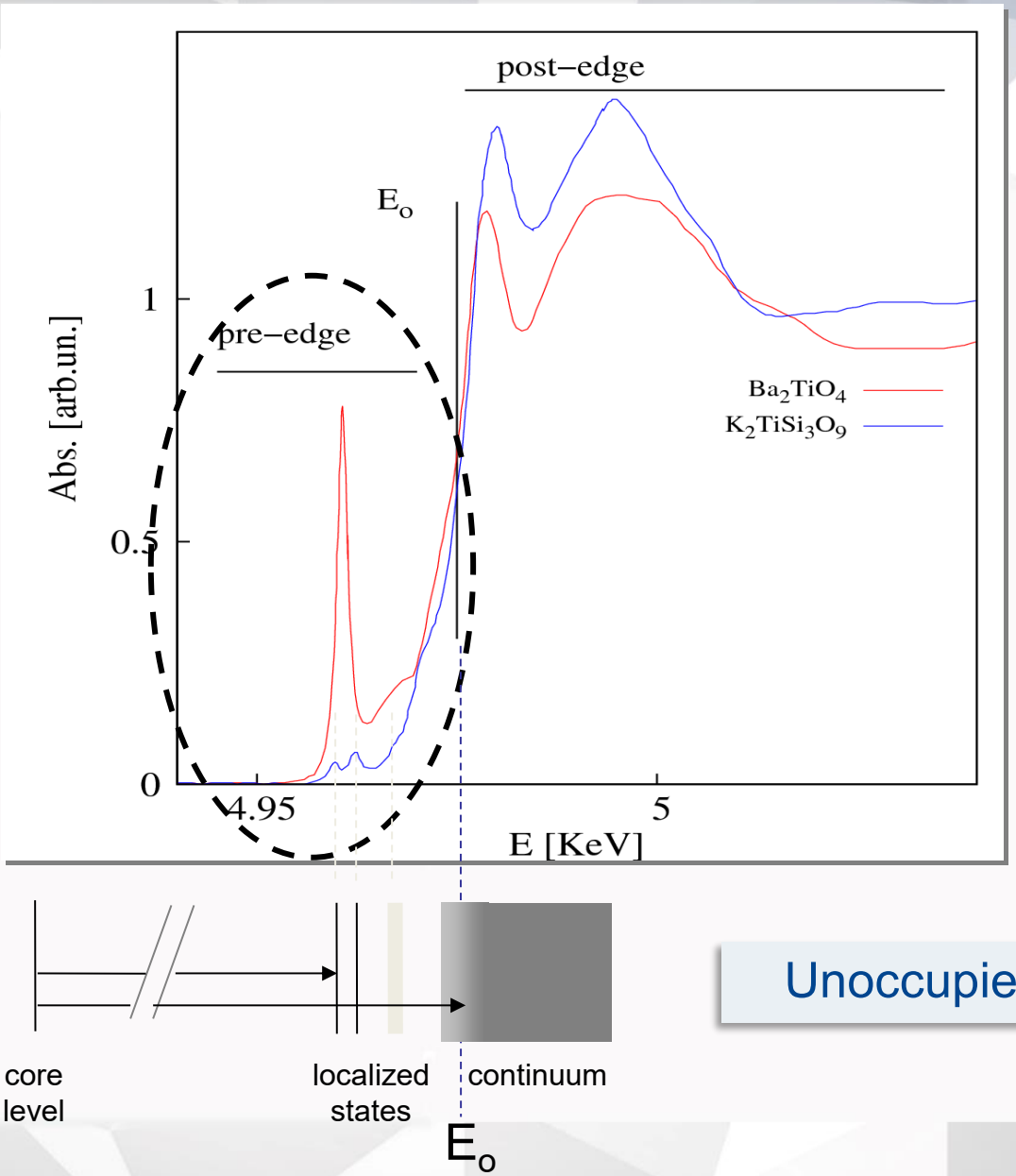


Pre-edge transitions in condensed matter

Pre-edge transitions probe low-lying unoccupied states with local orbital character.

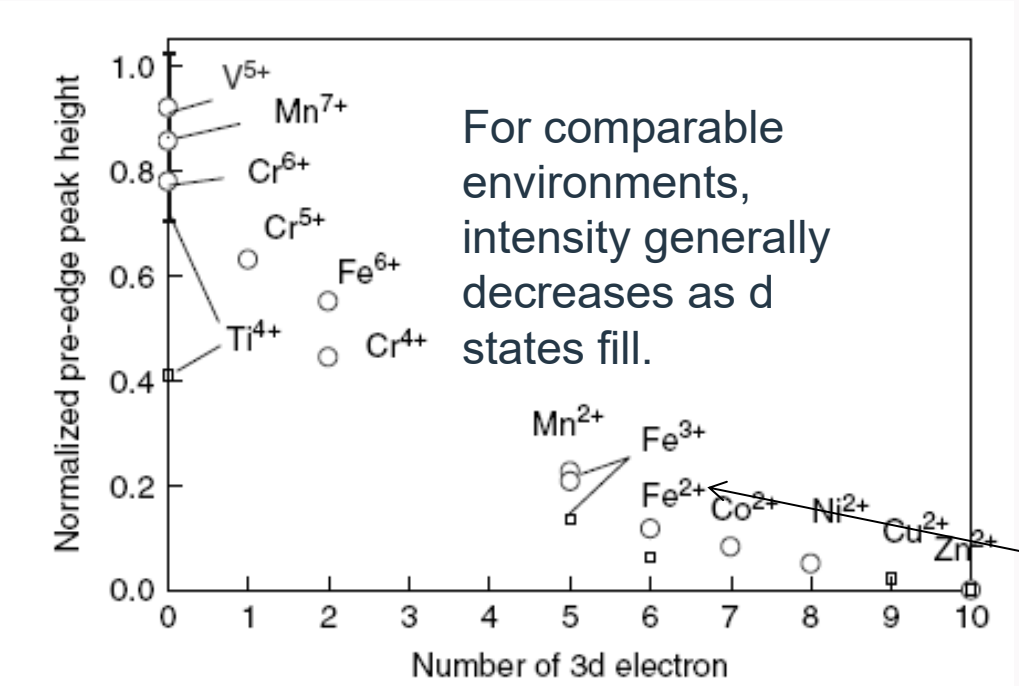
XANES complements XPS:

XANES probes **unoccupied** states, while valence-band **XPS** probes **occupied** states.



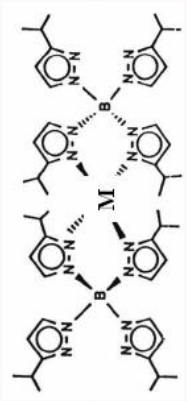
Unoccupied states

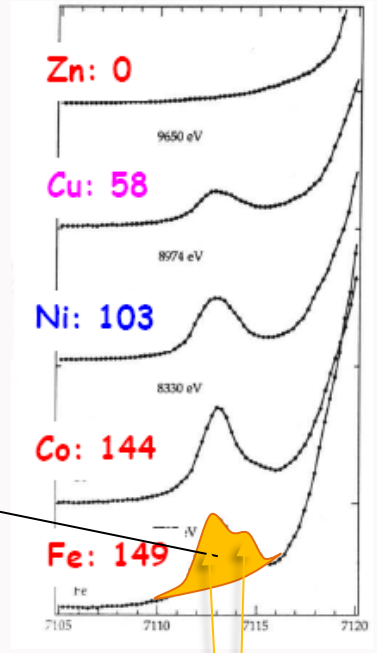
3d-metal K *pre*-edges: intensity and d-state occupancy

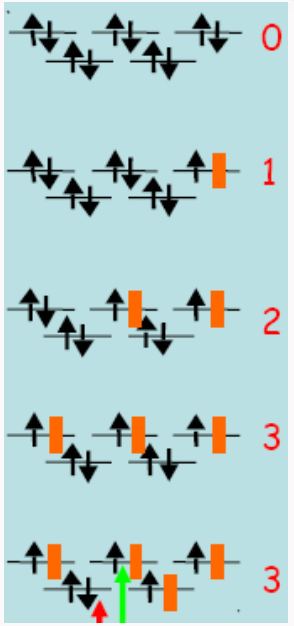


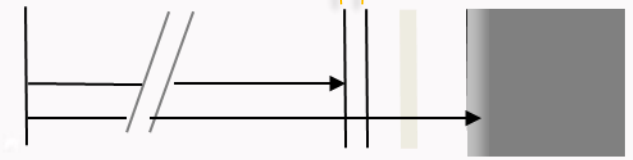
K pre-edges probe states with **3d character**.

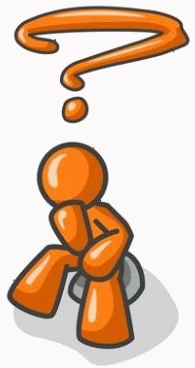
Example: pseudo-tetrahedral metal complexes $M(B(3\text{-isopropyl-pyrazol-1-yl})_4)_2$





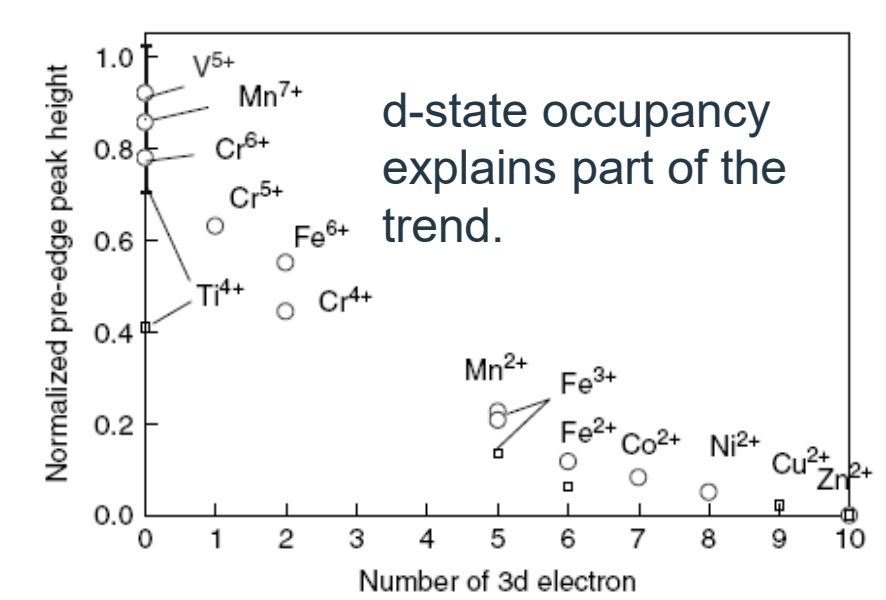


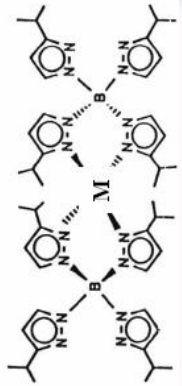


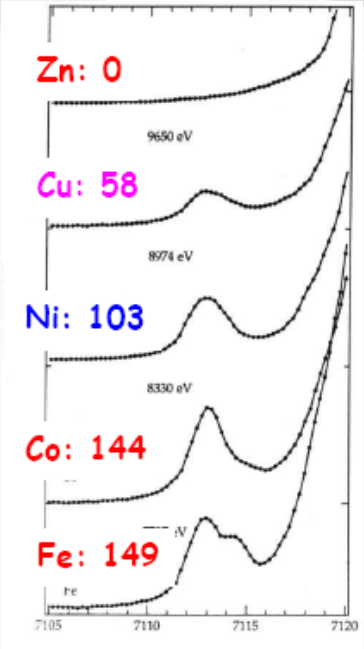


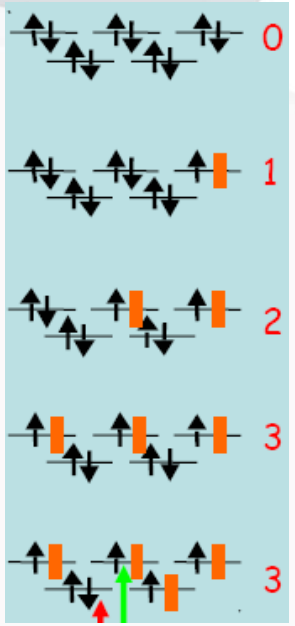
But...
These are 3d states!

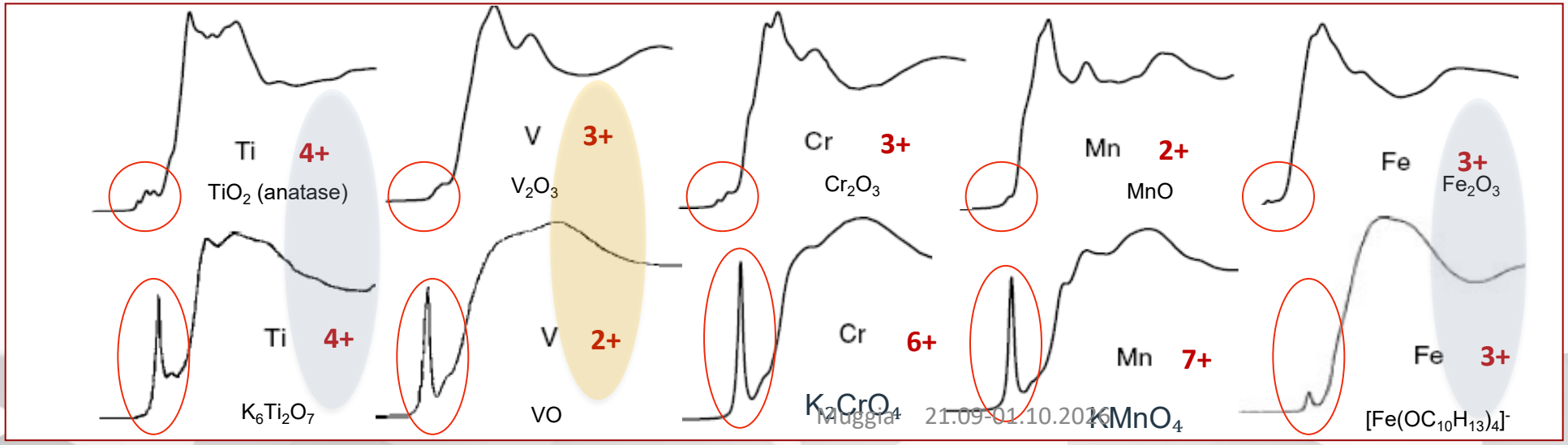
Pre-edge intensity also depends on coordination







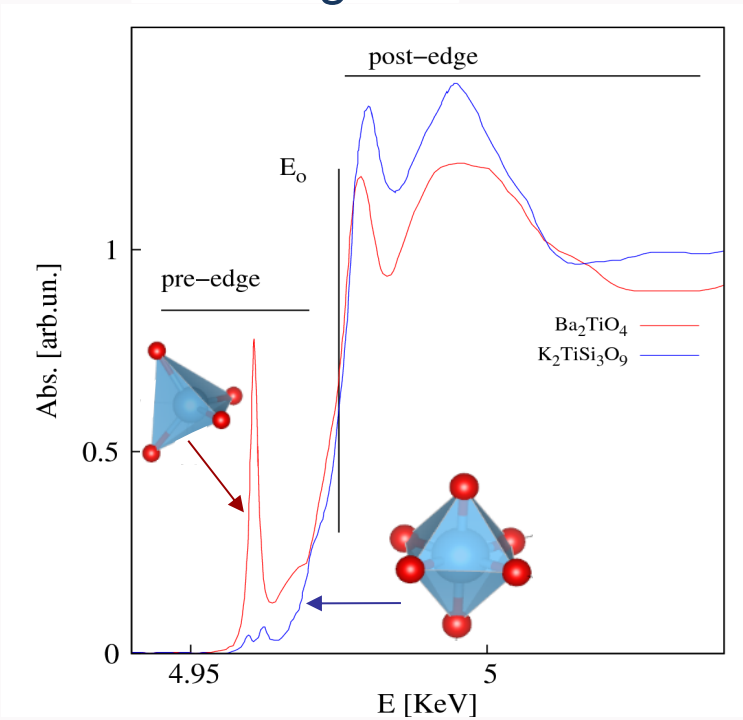




Large differences also for absorbers with the **same oxidation state**

Local coordination shapes the pre-edge spectrum

Ti K edge

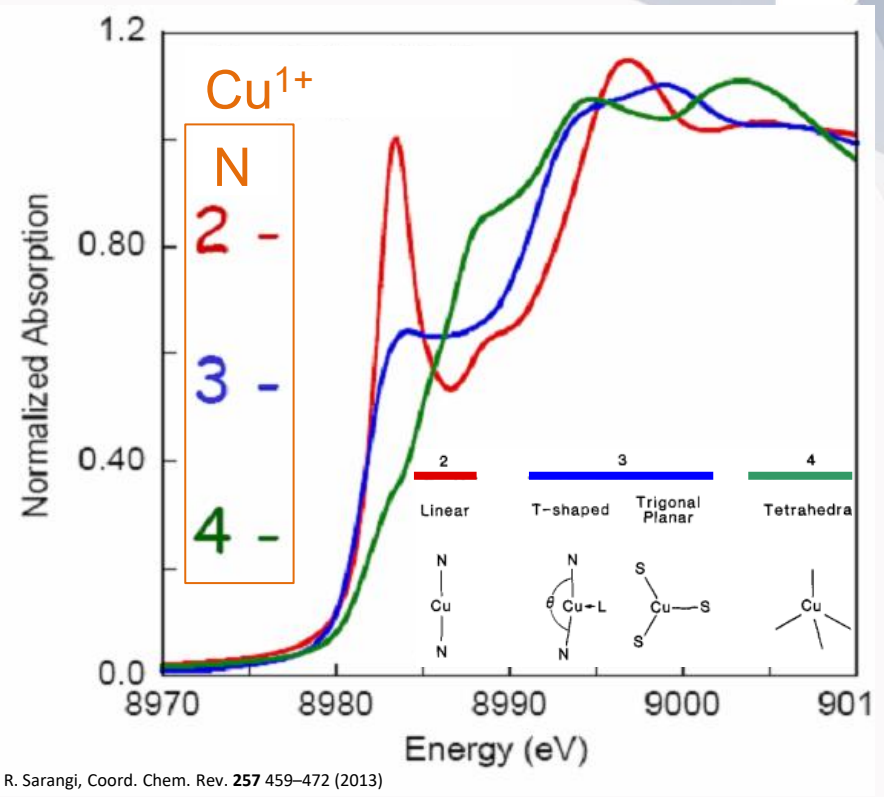


The **same element** in the **same oxidation** state can show **different XANES features** in different compounds…

…as a function of **coordination geometry** and **bonding**

The XANES features are **fingerprints for specific compounds**

Cu K edge



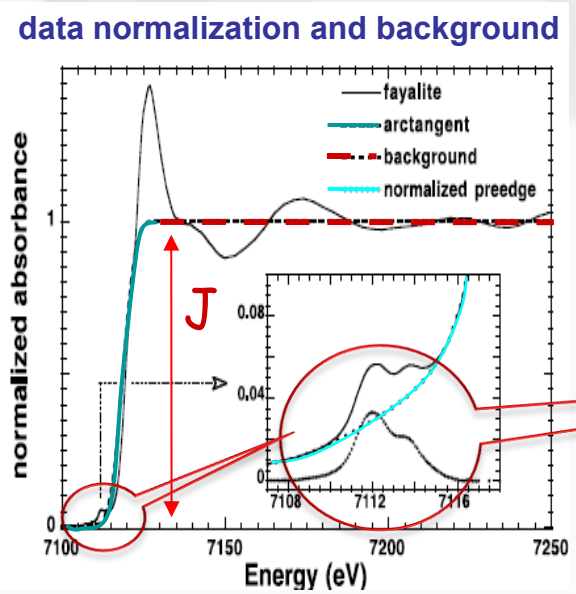
R. Sarangi, Coord. Chem. Rev. **257** 459–472 (2013)

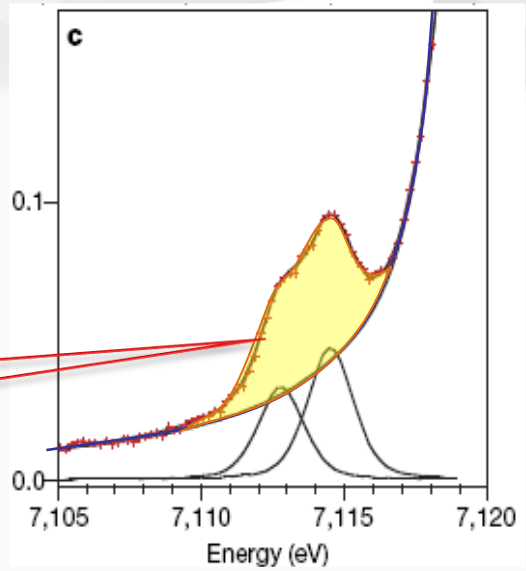
Extracting pre-edge features

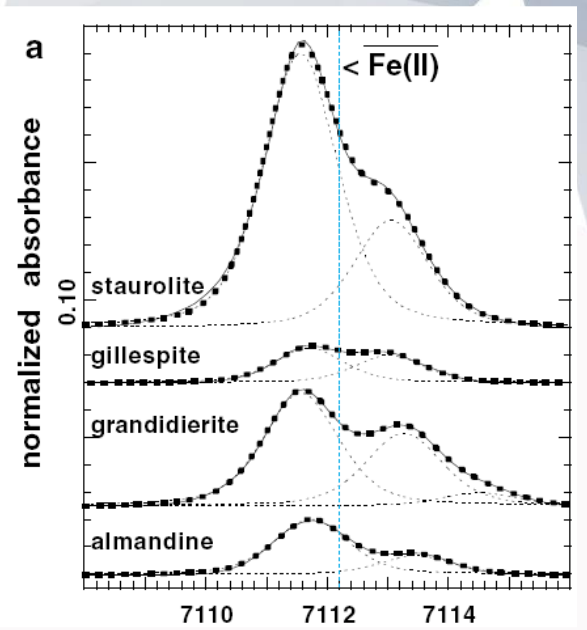
M. Wilke, F. Farges et al.

American Mineralogist, Volume 86, pages 714–730, 2001

data normalization and background





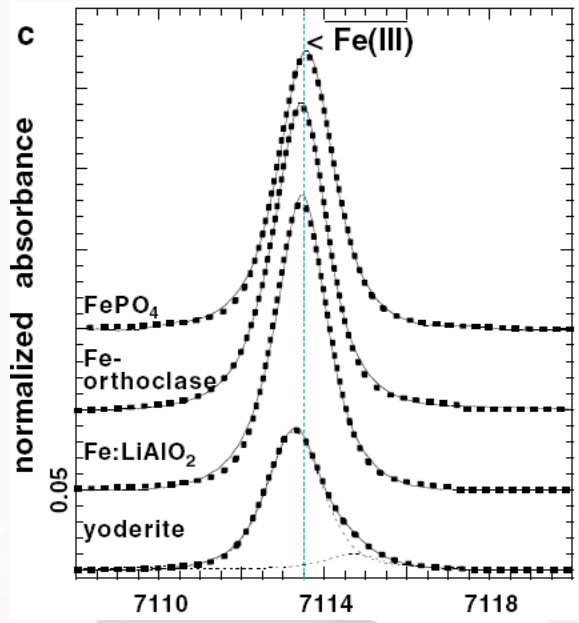


Pre-edge analysis: a practical workflow

1. Normalize the absorption edge to Δμ = 1.
2. Fit the rising-edge background with an appropriate smooth function.
3. Fit the pre-edge peaks and extract **area**, **centroid** and **width**.

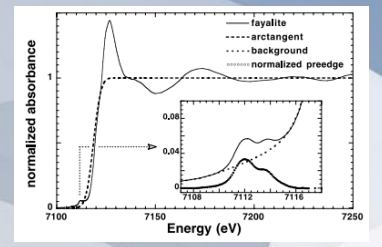
A *Voigt* profile convolves **Lorentzian lifetime** broadening with **Gaussian instrumental** broadening.

A pseudo-Voigt approximates this profile.

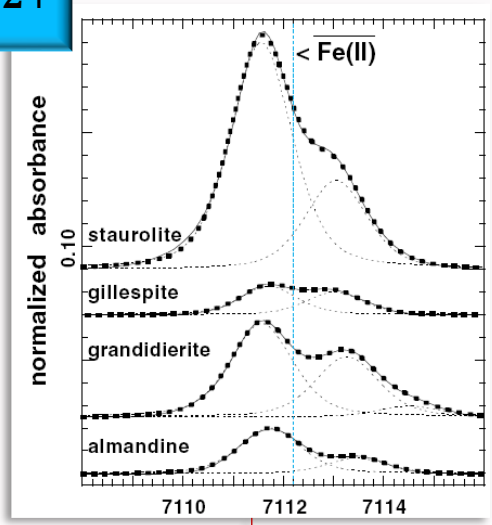


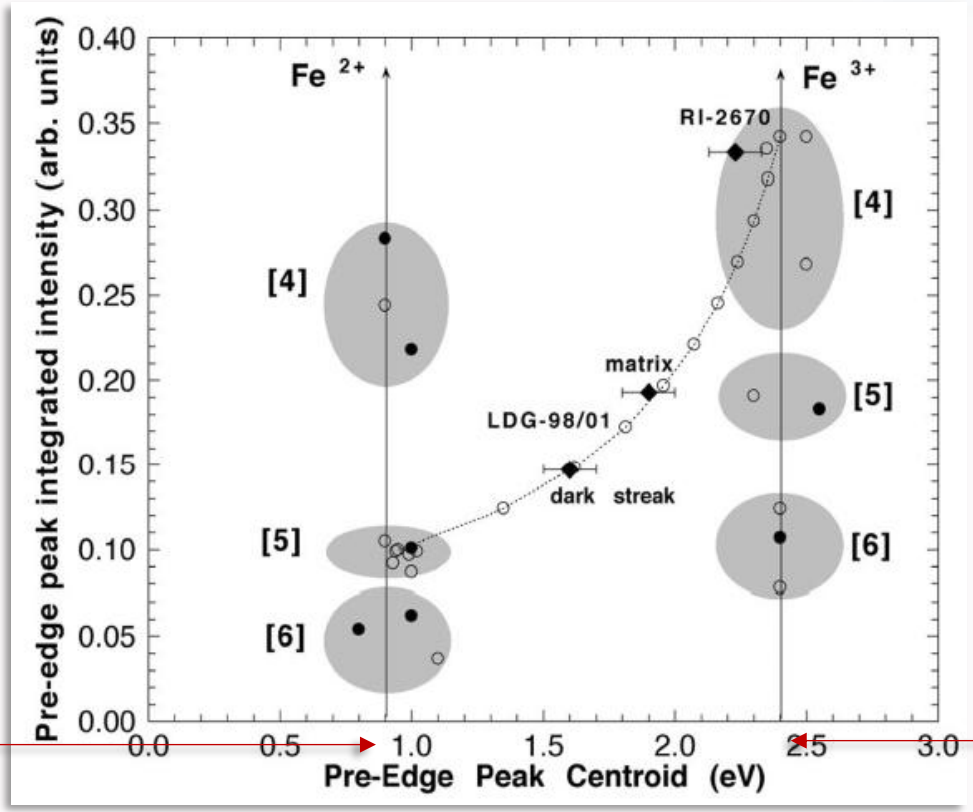
Fe pre-edge: oxidation state and coordination

Reference-based interpretation

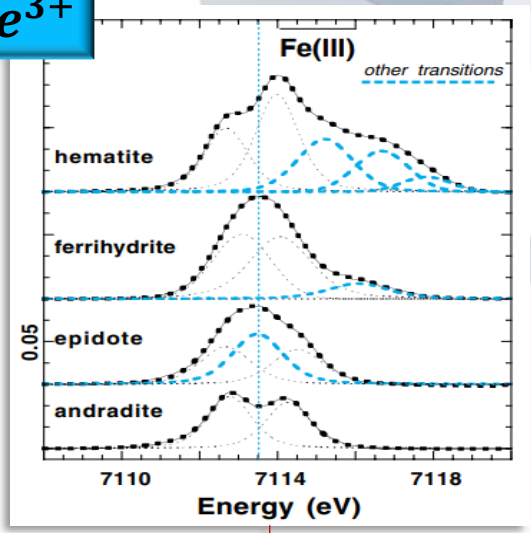


Fe^{2+}





Fe^{3+}



Calibration with reference compounds

Area: sensitive to coordination **number** & **symmetry**
Centroid: sensitive to **oxidation state**

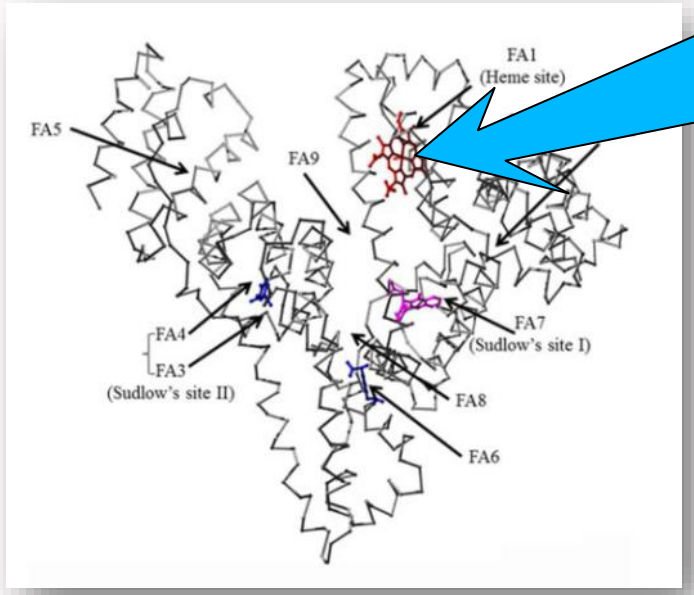
American Mineralogist, Volume 86, pages 714–730, 2001

Oxidation state and coordination of Fe in minerals: An Fe *K*-XANES spectroscopic study

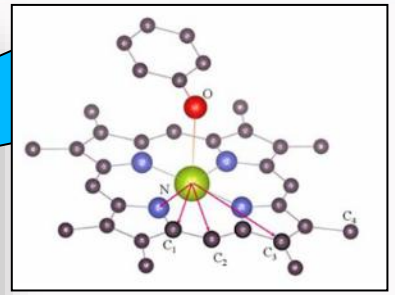
MAX WILKE,[1,*] FRANÇOIS FARGES,[1,2] PIERRE-EMMANUEL PETIT,[3] GORDON E. BROWN JR.,[2,4] AND FRANÇOIS MARTIN[5]

Fe in heme–albumin: drug-induced coordination changes

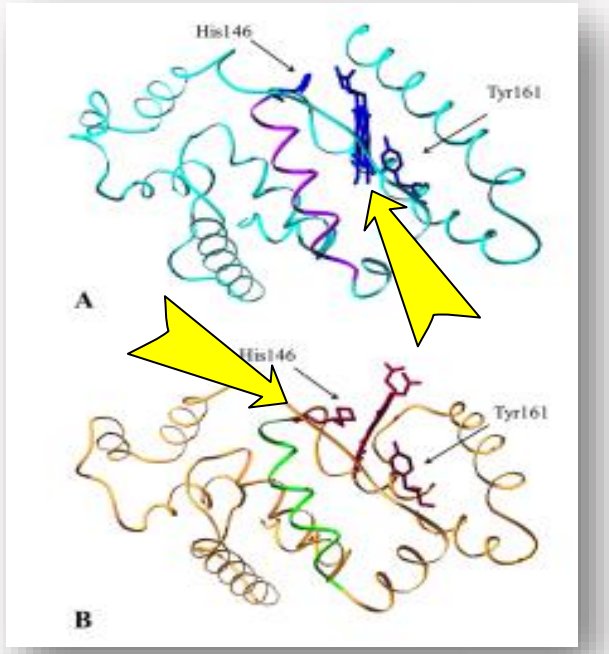
Biophysics

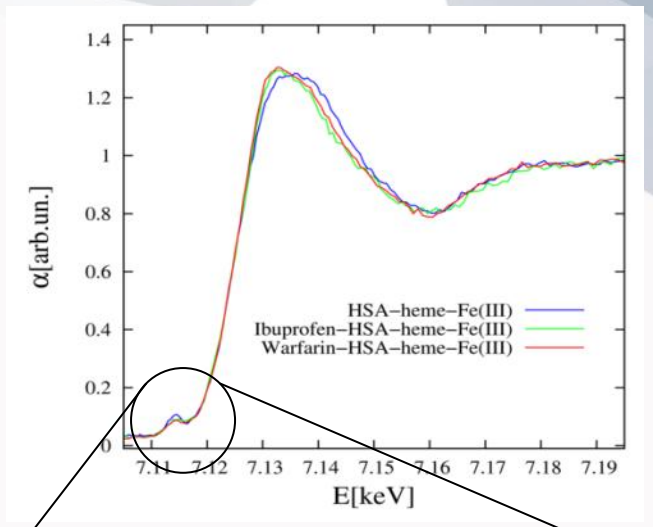


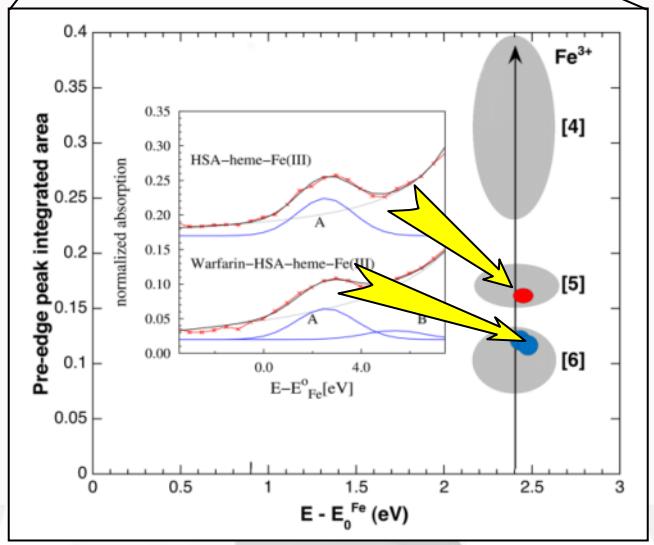
Human serum albumin (HSA)



Heme Fe: five- or six-coordinated







OPEN ACCESS Freely available online PLOS ONE

The Five-To-Six-Coordination Transition of Ferric Human Serum Heme-Albumin Is Allosterically-Modulated by Ibuprofen and Warfarin: A Combined XAS and MD Study

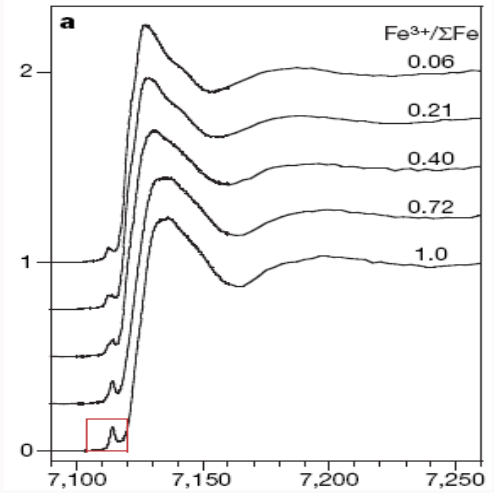
Carlo Meneghini[1*], Loris Leboffe[1,2*], Monica Bionducci[1], Gabriella Fanali[3], Massimiliano Meli[4], Giorgio Colombo[4], Mauro Fasano[3], Paolo Ascenzi[2,5*], Settimio Mobilio[1]

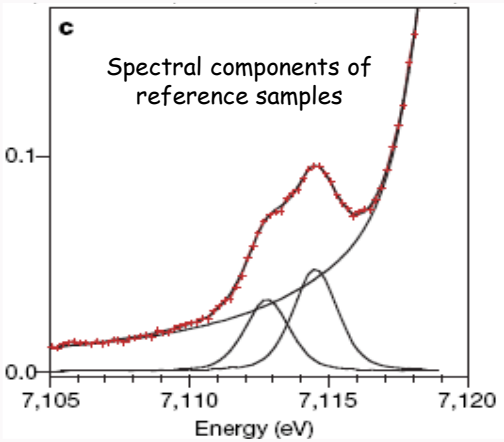
Fe speciation and Archaean mantle temperature

Geophysics

Geology

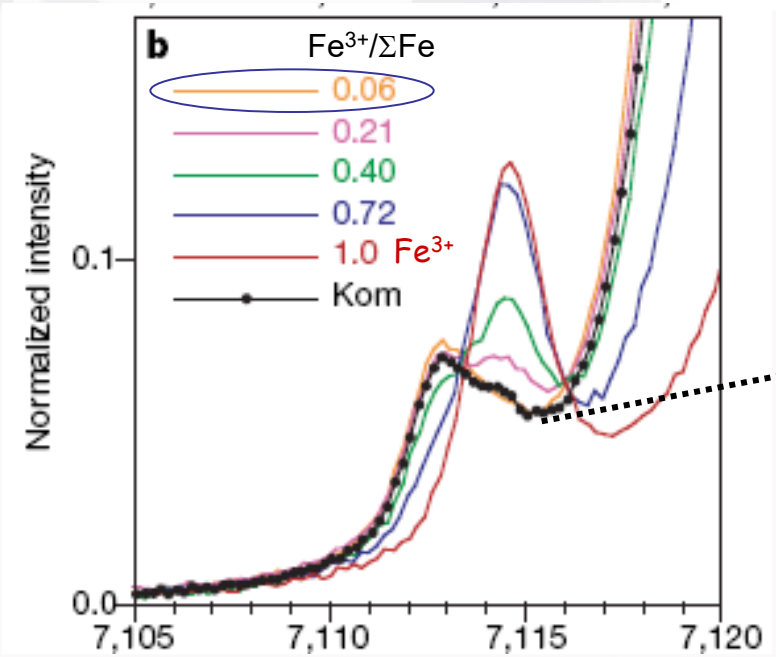
Reference samples with different $Fe^{3+}/\Sigma Fe$ ratios

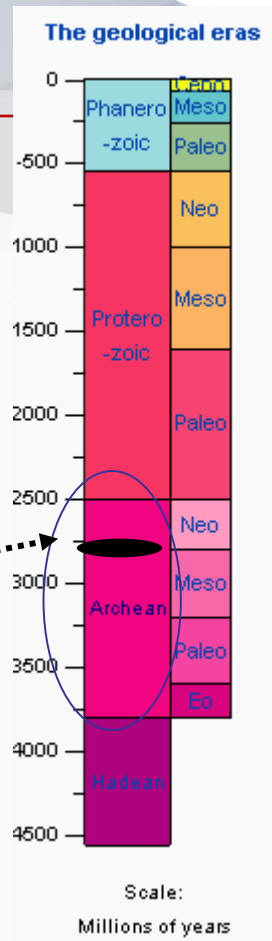




Andrew J. Berry

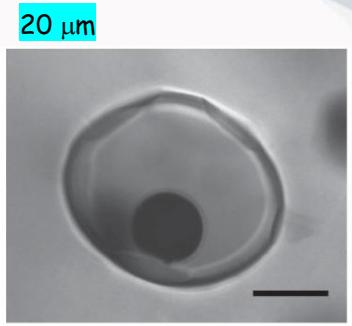
Vol 455|16 October 2008|doi:10.1038/nature07377





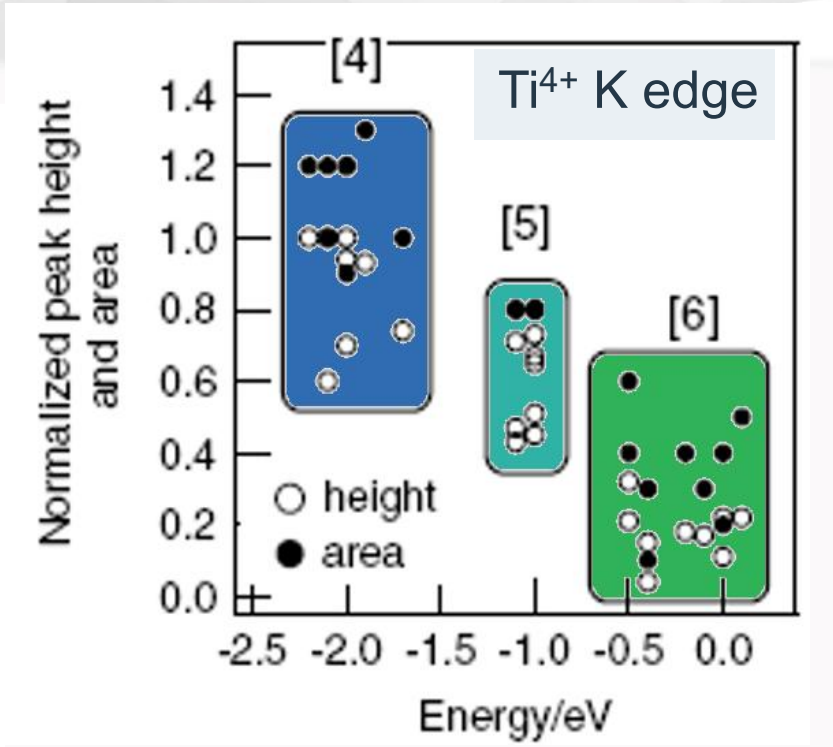
The $Fe^{3+}/\Sigma Fe$ analysis supports the formation of Belingwe komatiites (about 1700 °C), **at very high mantle temperatures** rather than hydrous melting.

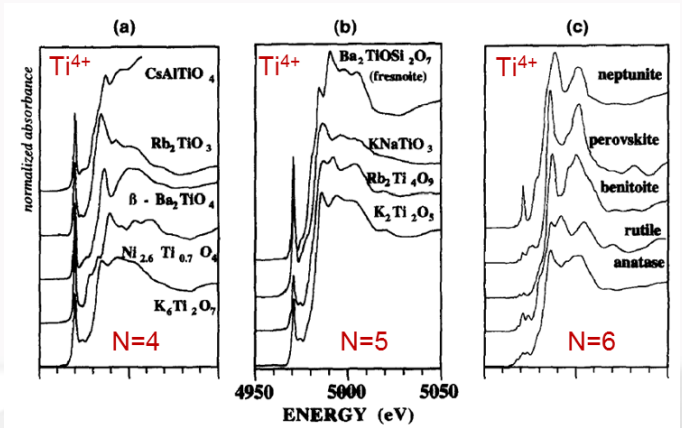
…



Belingwe komatiite inclusions in olivine
Diameter ≈ 15 µm

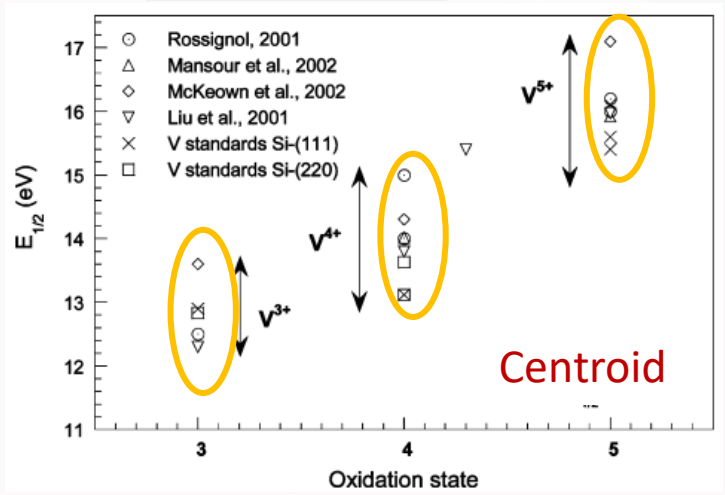
pre-edge: sensitivity to coordination geometry

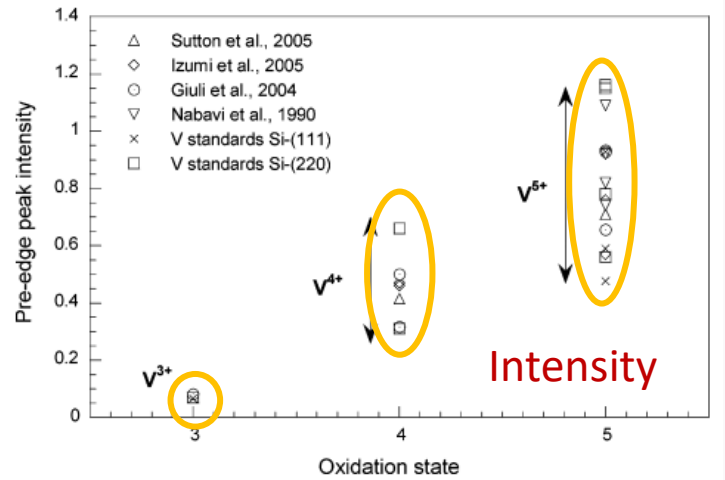


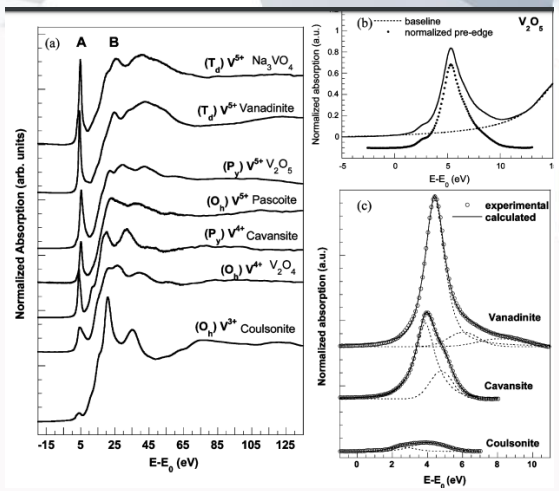


6. Farges F, Brown GE, Rehr JJ. *Geochim. Cosmochim. Acta* 1996; 60: 3023.

V K edge

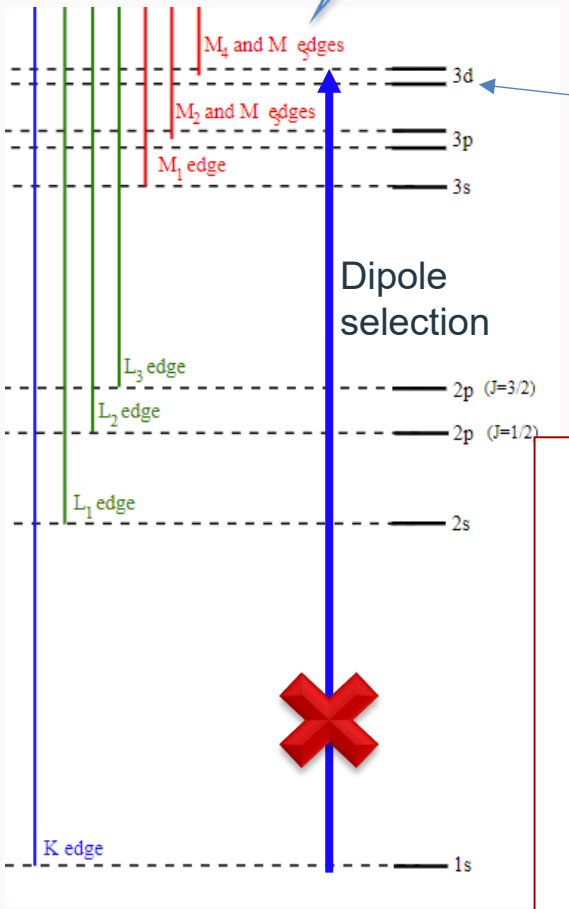




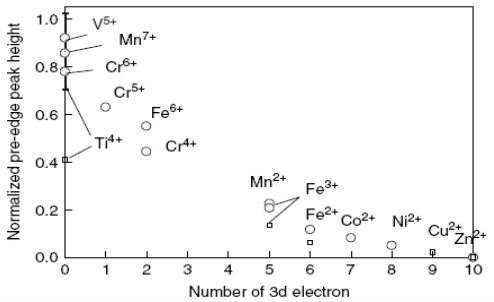


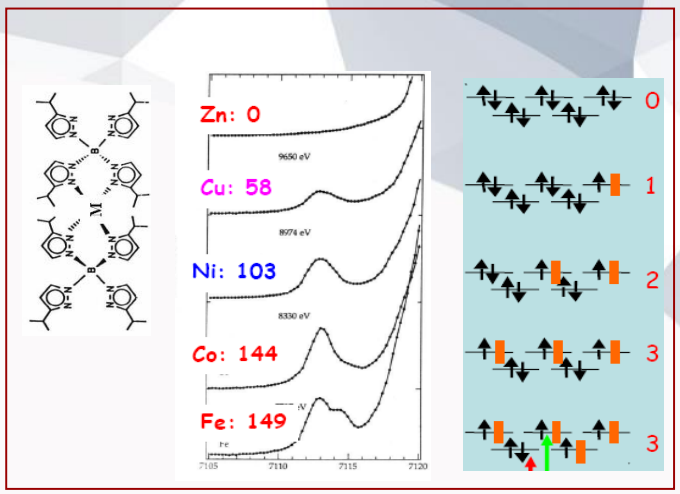
J. Phys. Chem. B **2007,** *111,* 5101−5110

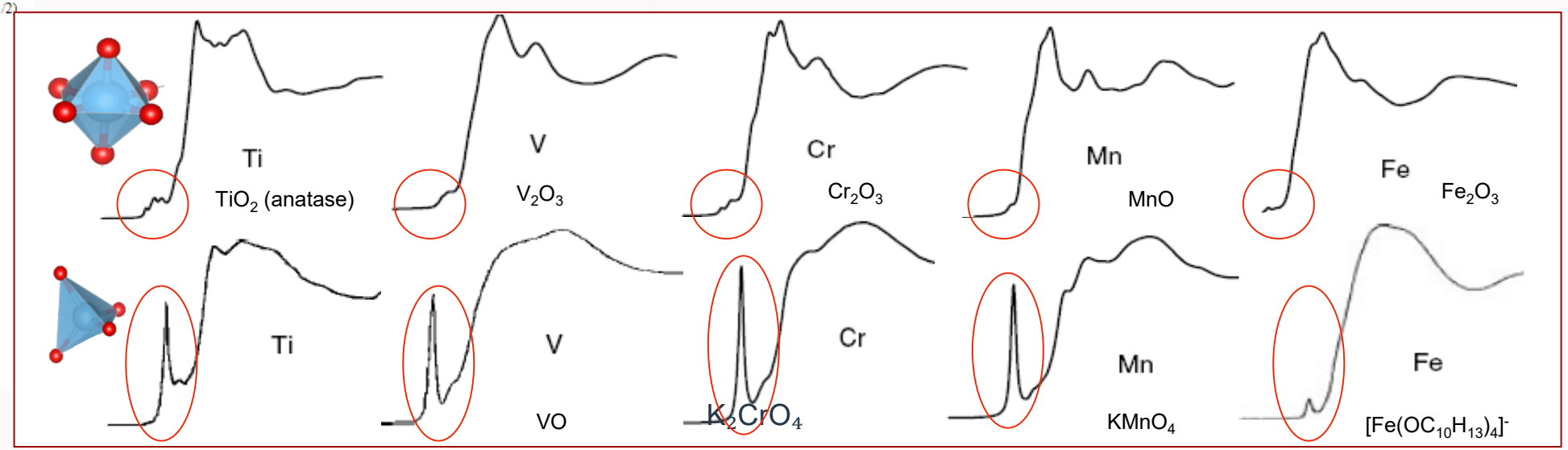
Why are 3d-metal K pre-edges dipole-active?



1s–3d: what allows the transition?







K-edge selection rules and p–d mixing

$$\frac{I_{s\to d}}{I_{s\to p}} \simeq 10^{-2}$$

p–d mixing provides p character to 3d-derived states, enabling dipole intensity from the 1s level.

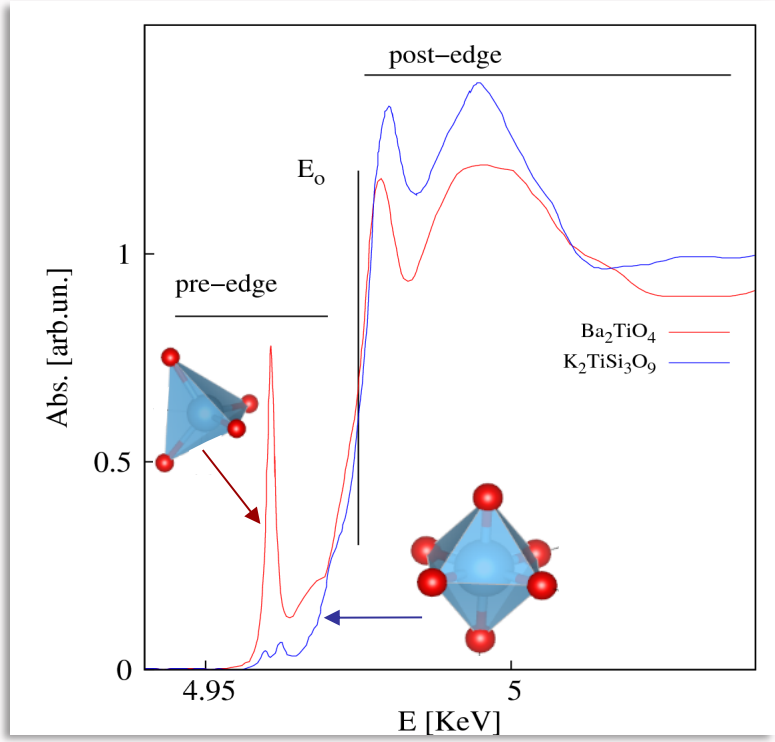
Table 1. Lists of irreducible representations and the relating functions in T_d, O_h, and D_{4h} point groups

T_d	p	d
A_1		$x^2+y^2+z^2$
A_2		
E		$(2z^2-x^2-y^2, x^2-y^2)$
T_1	(R_x, R_y, R_z)	
T_2	(x, y, z)	(xz, yz, xy)

O_h	p	d
A_{1g}		$x^2+y^2+z^2$
A_{2g}		
E_g		$(2z^2-x^2-y^2, x^2-y^2)$
T_{1g}	(R_x, R_y, R_z)	
T_{2g}		(xz, yz, xy)
A_{1u}		
A_{2u}		
E_u		
T_{1u}	(x, y, z)	
T_{2u}		

Yamamoto X-Ray Spectrom. 2008; **37**: 572–584

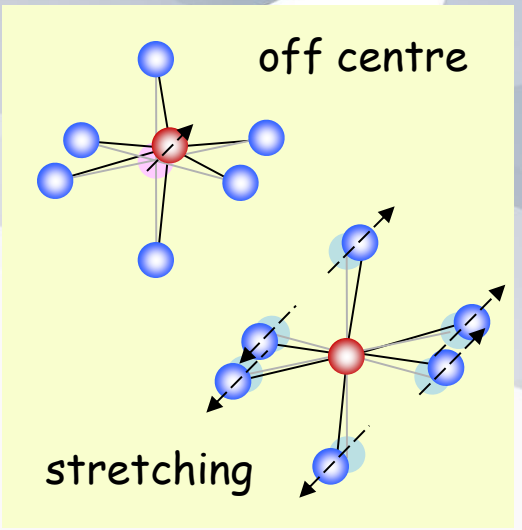
Inversion symmetry forbids on-site p–d mixing.



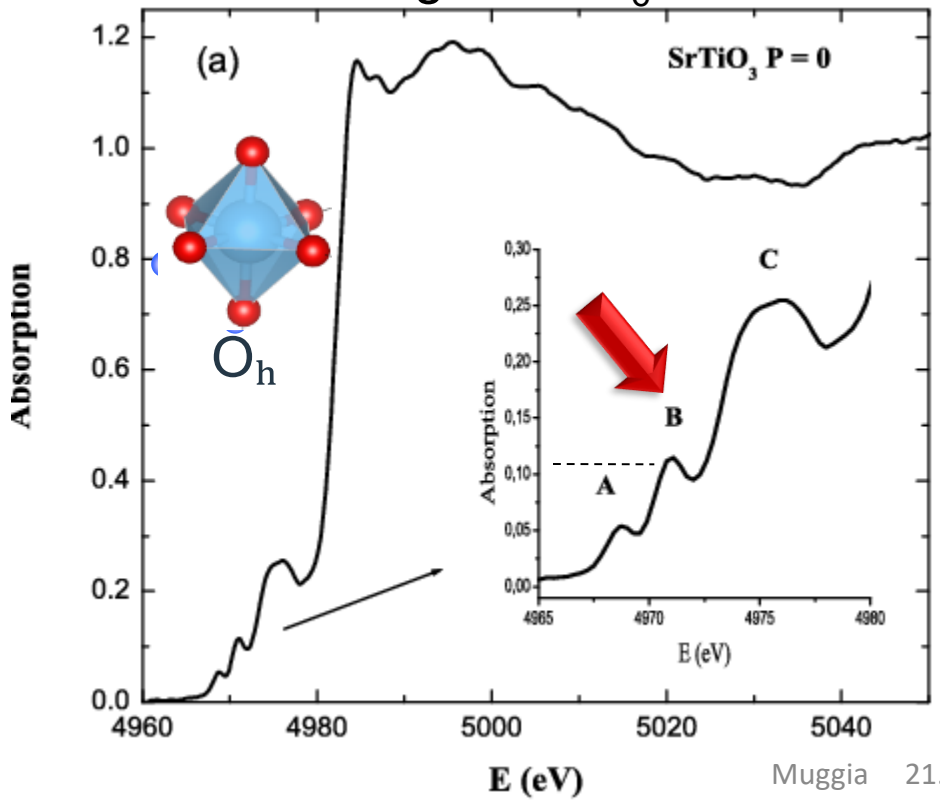
Pre-edge intensity probes local coordination symmetry.

Local symmetry and p–d mixing in TiO_6

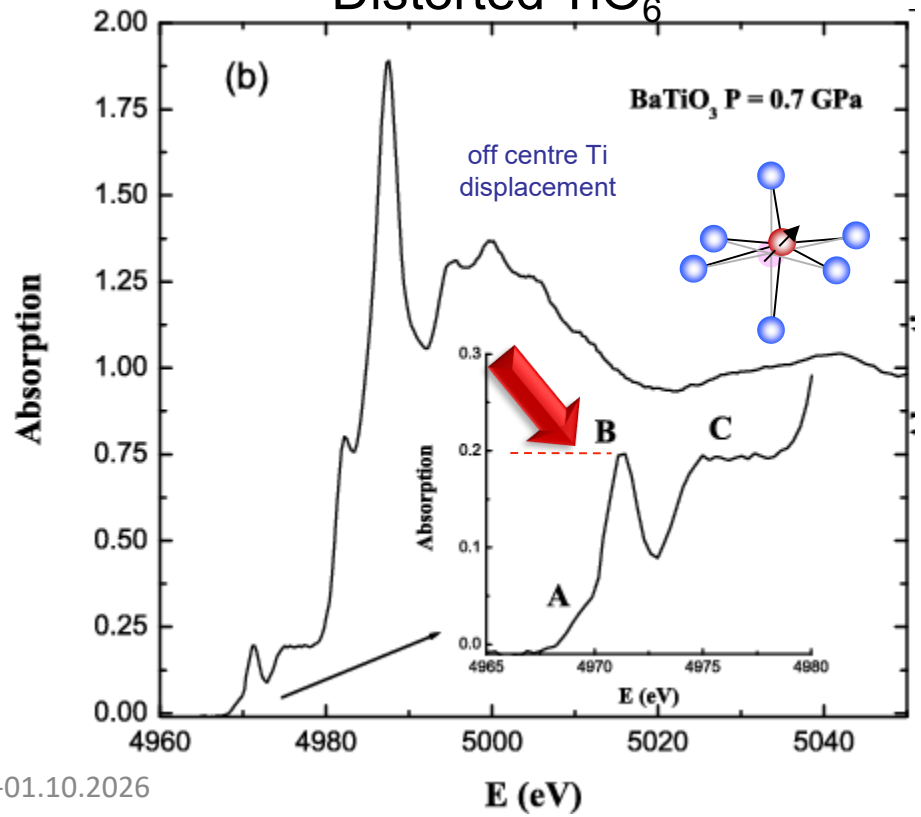
Ti off-centering breaks inversion symmetry and allows on-site p–d mixing, enhancing pre-edge intensity. Distortion matters when it changes the relevant symmetry.



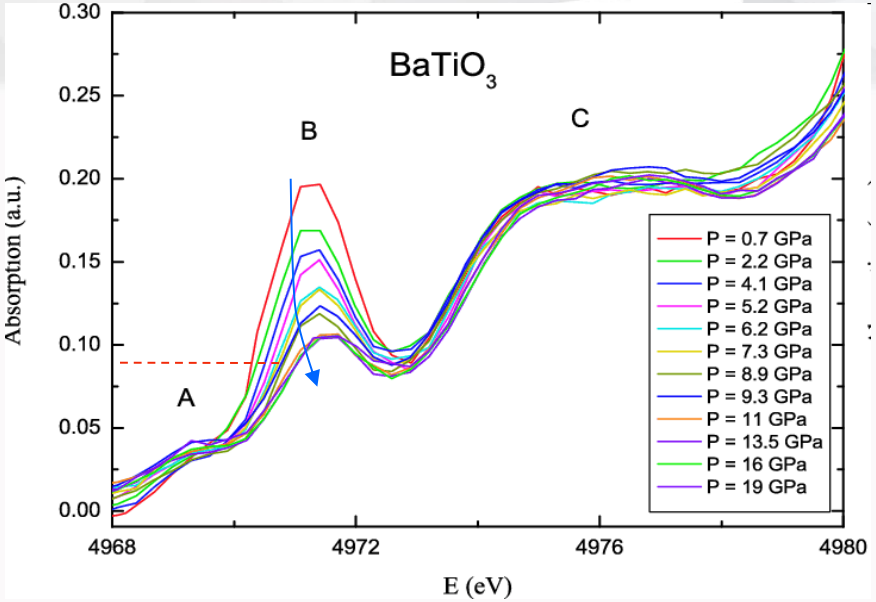
Regular TiO_6



Distorted TiO_6

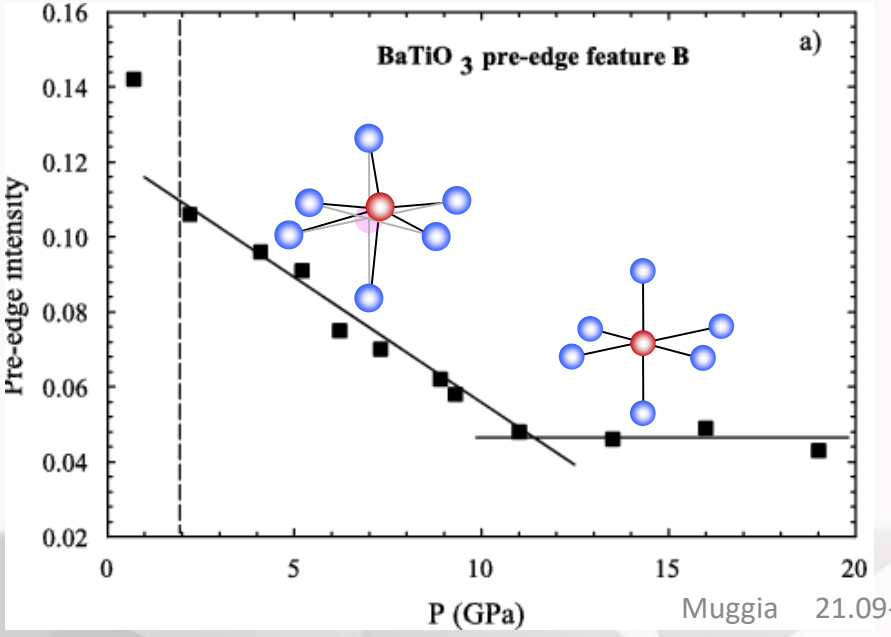


Pressure, Ti off-centering and ferroelectricity in $BaTiO_3$



Peak B weakens as pressure reduces Ti off-centering.

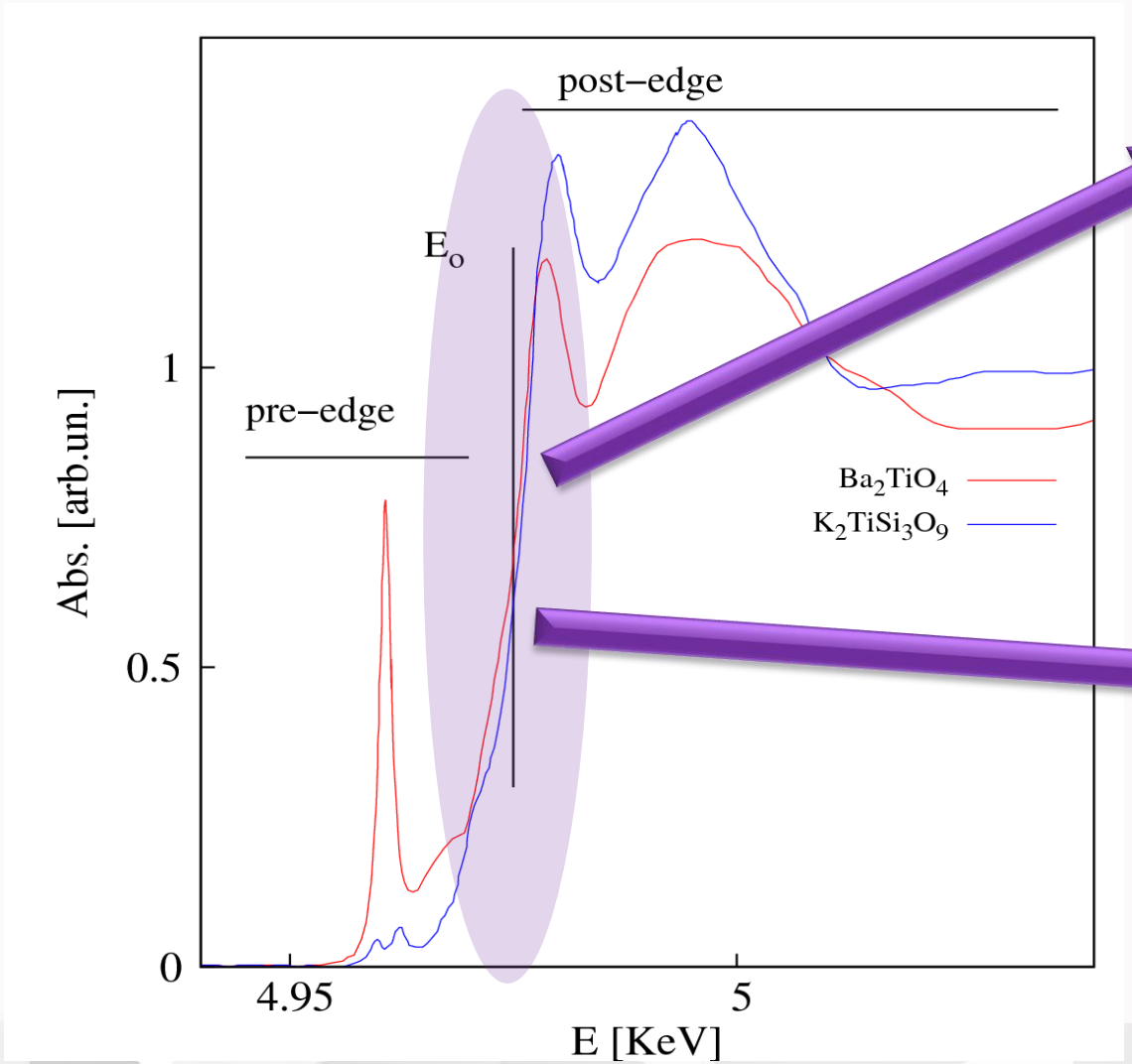
Above about 10 GPa, the weak B feature is consistent with a nearly centrosymmetric Ti environment and reduced on-site Ti *pd* mixing.



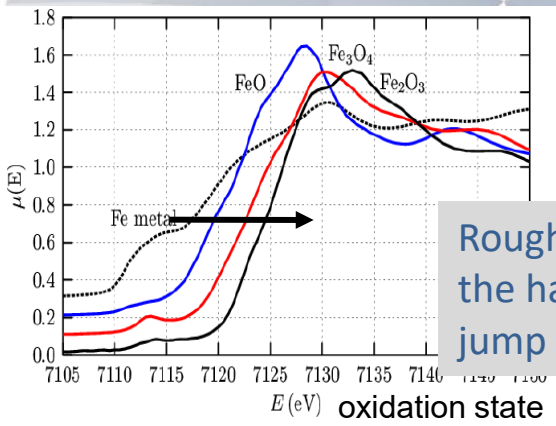
Europhys. Lett., **74** (4), pp. 706–711 (2006)
DOI: 10.1209/epl/i2006-10020-2 J. P. Itié et al.

The absorption edge:

position and shape

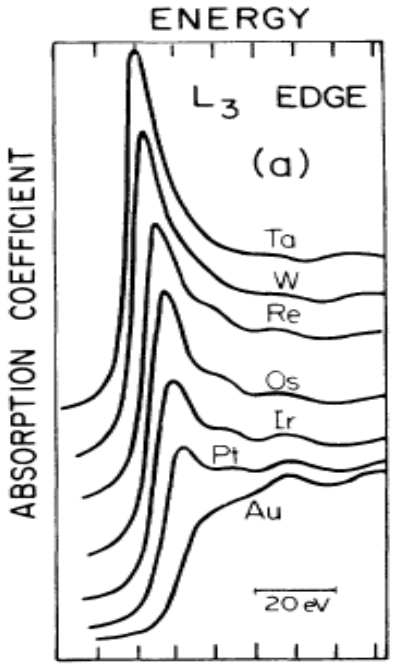


Edge position



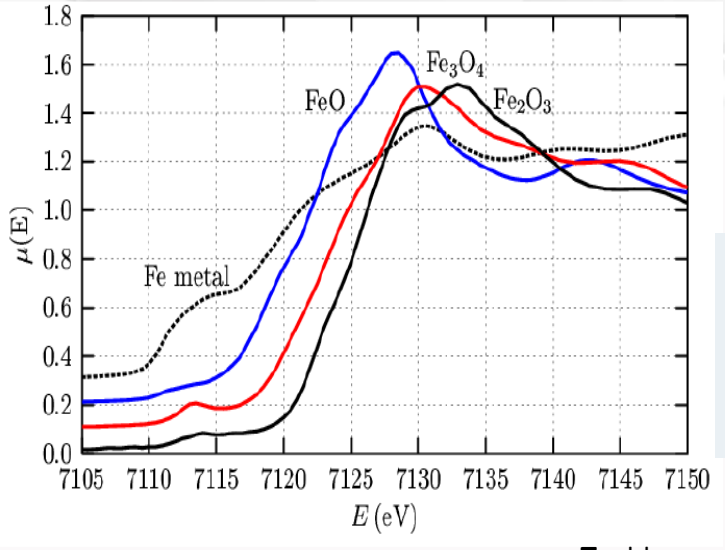
Roughly correspond to the half of the edge jump discontinuity

Edge shape

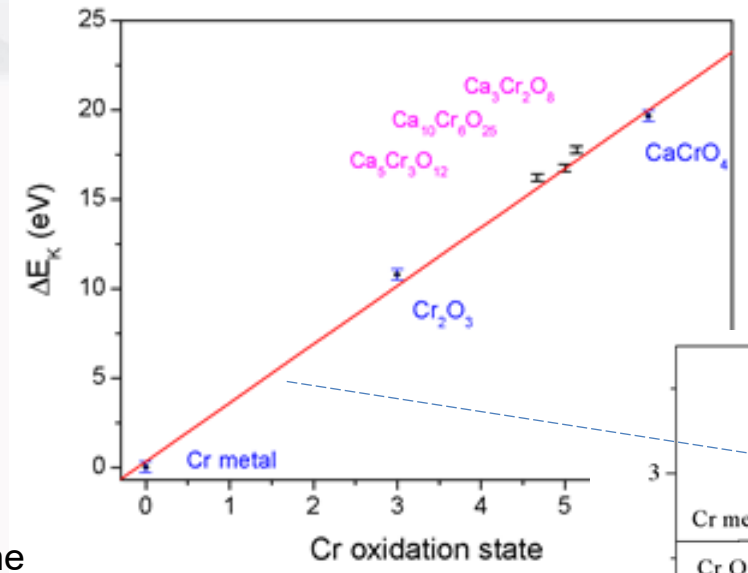


L edges of 4d and 5d elements

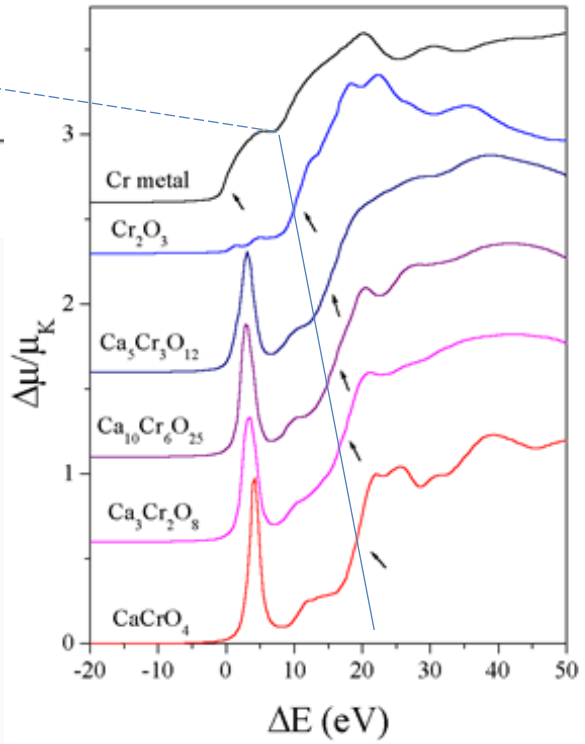
Chemical shifts and oxidation state

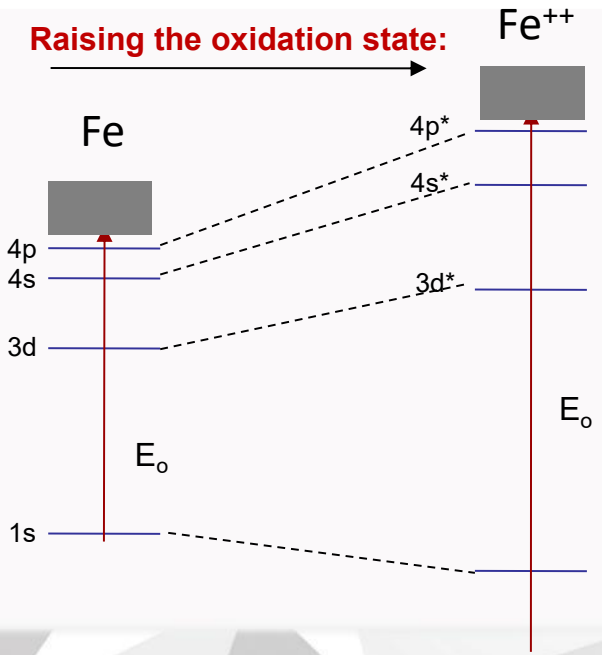


Higher oxidation state raises the edge energy



Cr K edge





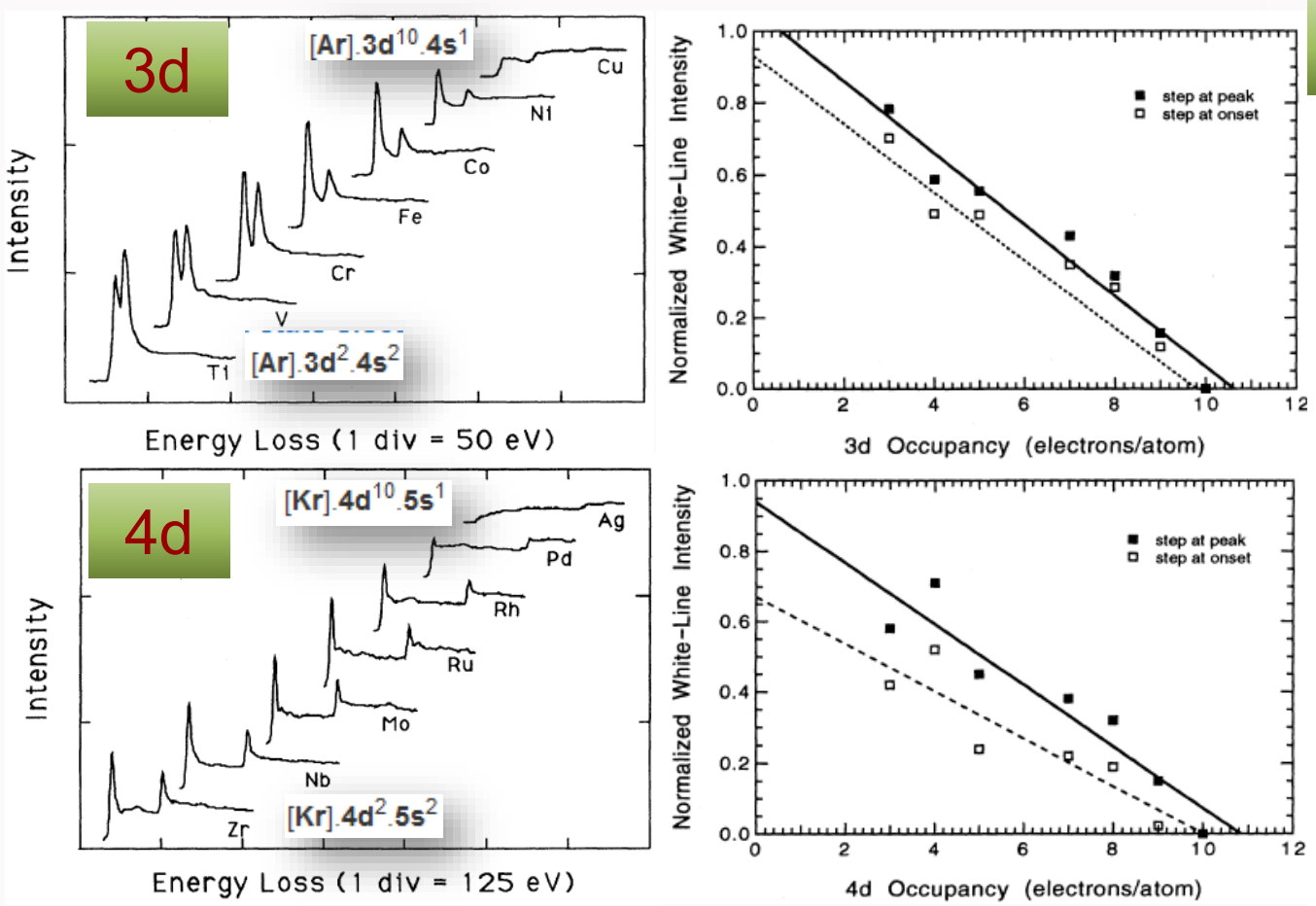
destabilizes the antibonding (**empty**) levels and onset of the continuum states

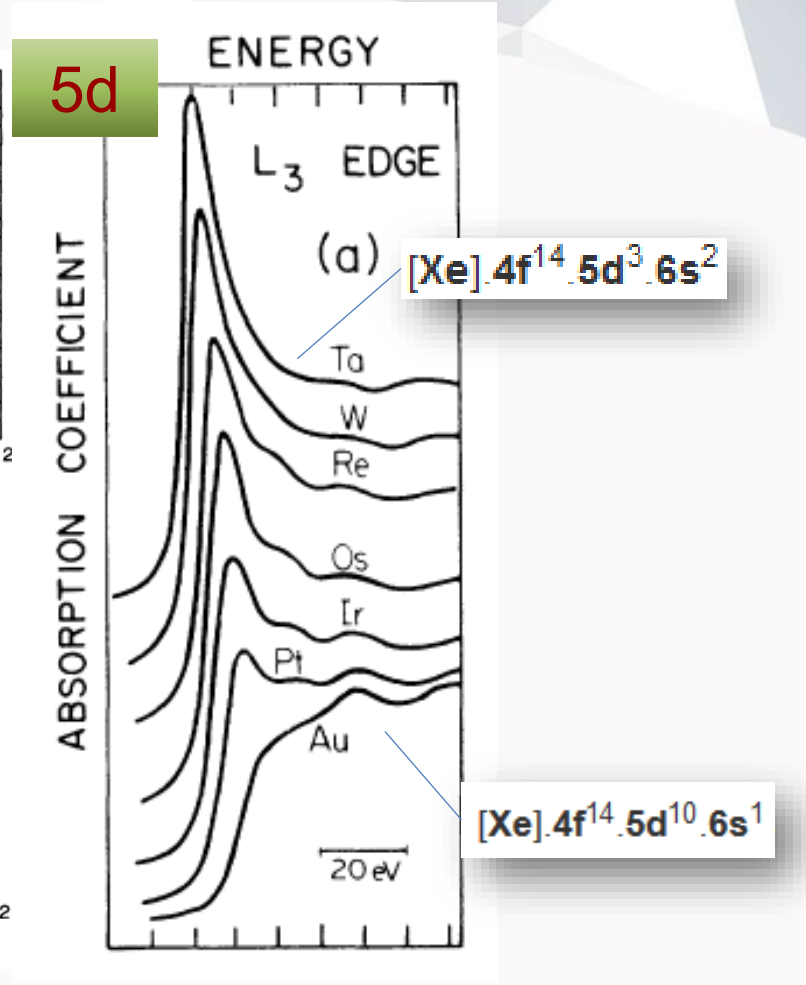
Oxidation often shortens metal–ligand bonds.

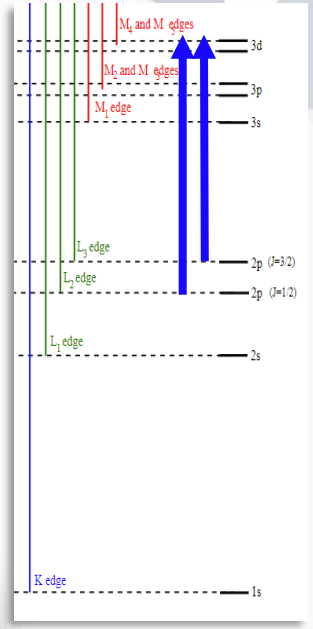
Reduces the screening stabilizing the core levels

$L_{2,3}$ white lines and unoccupied d states

$L_{2,3}$ edges:
2p → nd transitions
(n = 3, 4, 5)







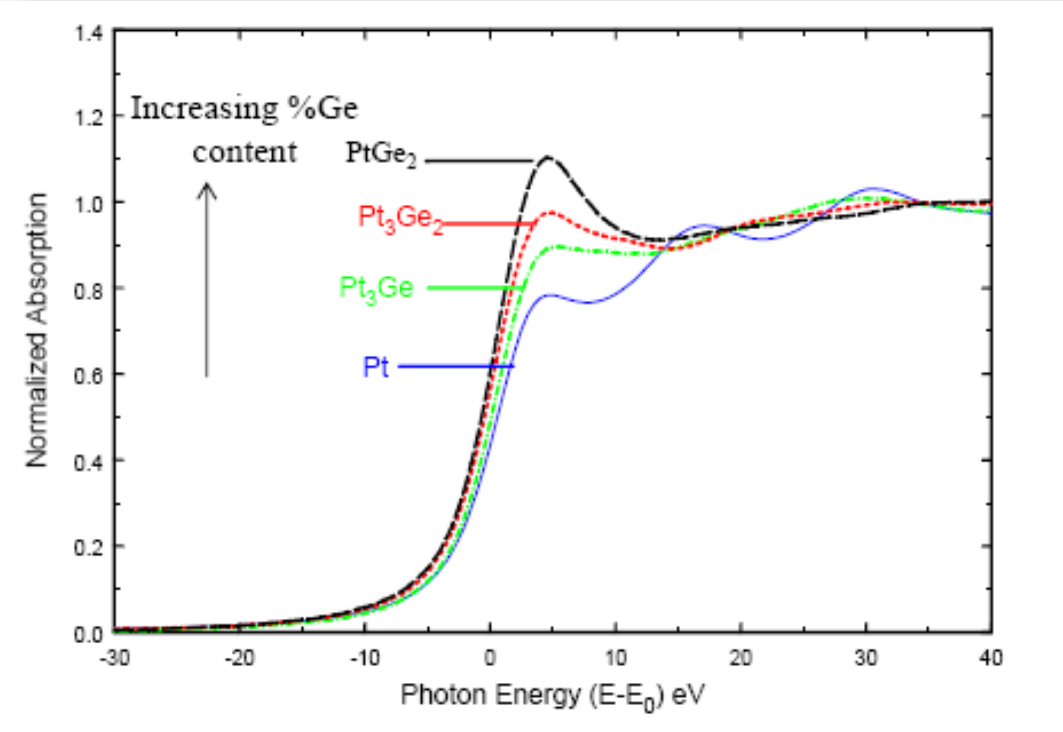
PHYSICAL REVIEW B VOLUME 47, NUMBER 14 1 APRIL 1993-II

White lines and *d*-electron occupancies for the 3*d* and 4*d* transition metals

D. H. Pearson,* C. C. Ahn, and B. Fultz

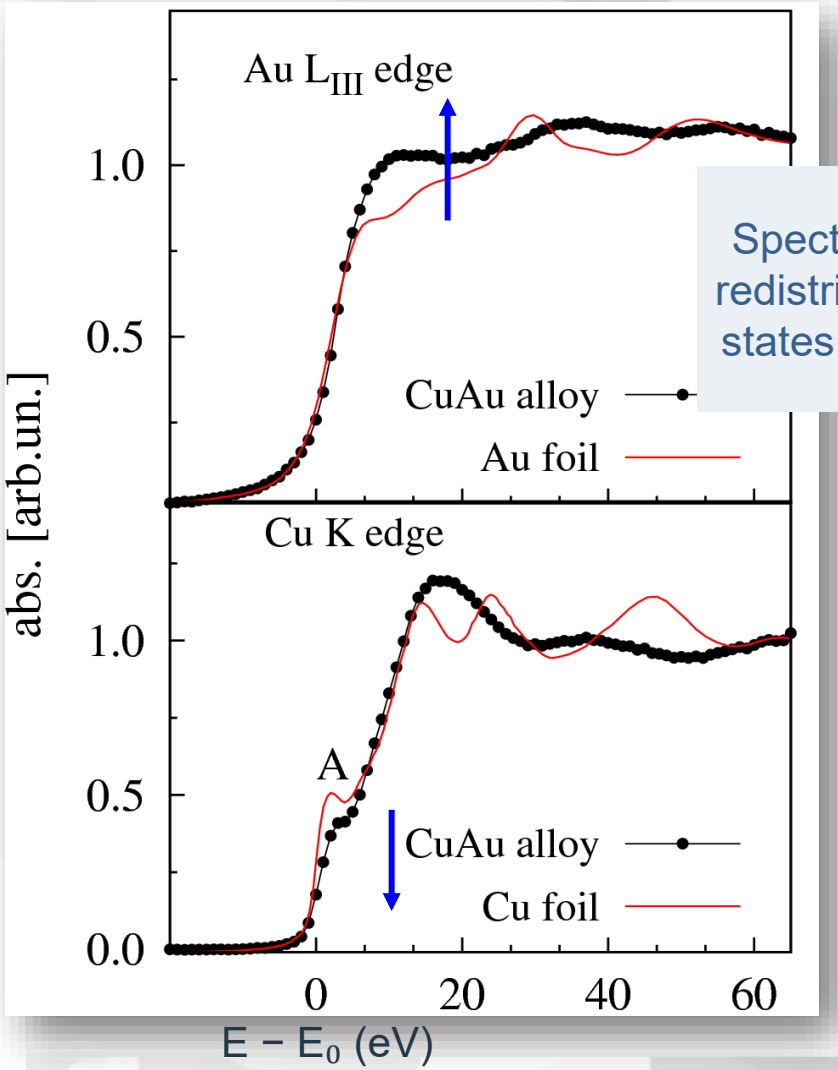
White-line changes in intermetallic compounds

Pt L_2 white line in Pt–Ge intermetallic compounds



- Transition is $2p$ to $5d$: Pt d-band full, so "no" intensity at edge.
- PtGe intermetallics: charge transfer from d-band of Pt to Ge, resulting in significant intensity at edge.
- Use as signature of Pt-Ge intermetallic formation.

Charge redistribution in Cu–Au alloys



Spectral changes indicate redistribution of unoccupied states between Au and Cu.

Chemical speciation in complex natural samples

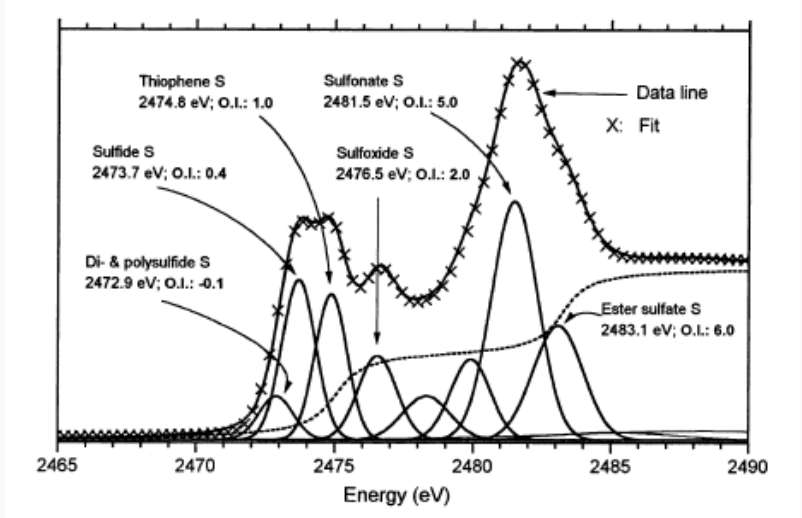
Applications in biology, geology, medicine, cultural heritage and chemistry

Natural samples are intrinsically complicated:

disordered, **multiphase**, **heterogeneous, and are often poorly knows composition**

Elemental analysis establishes composition, but does not necessarily identify chemical species.

XRD is insensitive to non-crystalline phases, amorphous components, non periodic structural or chemical defects, grain-boundary …



The XANES features provide fingerprints of ***specific chemical species*** *and* ***local environments***

Mixtures: linear combination analysis (LCA)

Environmental sciences

Fitting the sample XANES spectrum as a weighted sum of suitable reference compounds spectra.

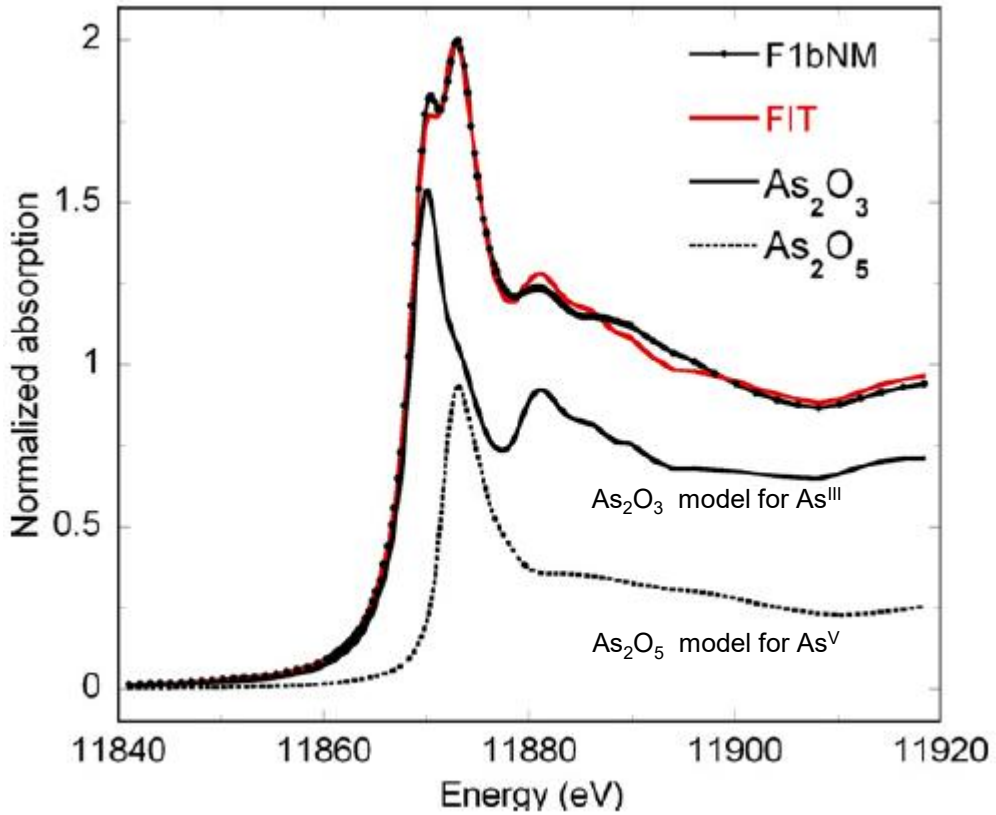
$$\mu^{th} = \sum_j \alpha_j \mu^{ref_j}$$

$$R^2 = \sum_i \left(\mu^{exp}(E_i) - \mu^{th}(E_i)\right)^2$$

α_j: absorber fraction represented by reference j

F. Bardelli et al. Geoch. & cosmochem. acta 2011

Arsenic adsorption in natural calcite

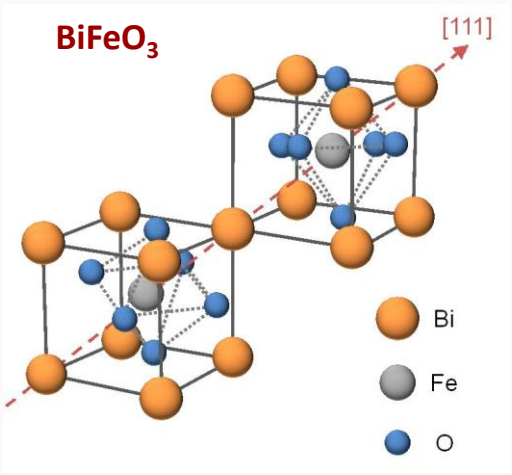


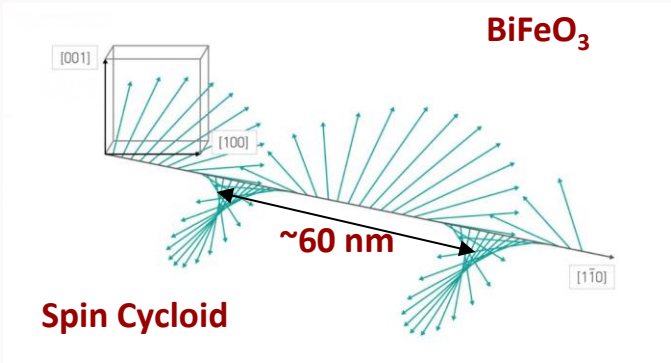
Magnetoelectric materials: local chemical homogeneity

Material sciences

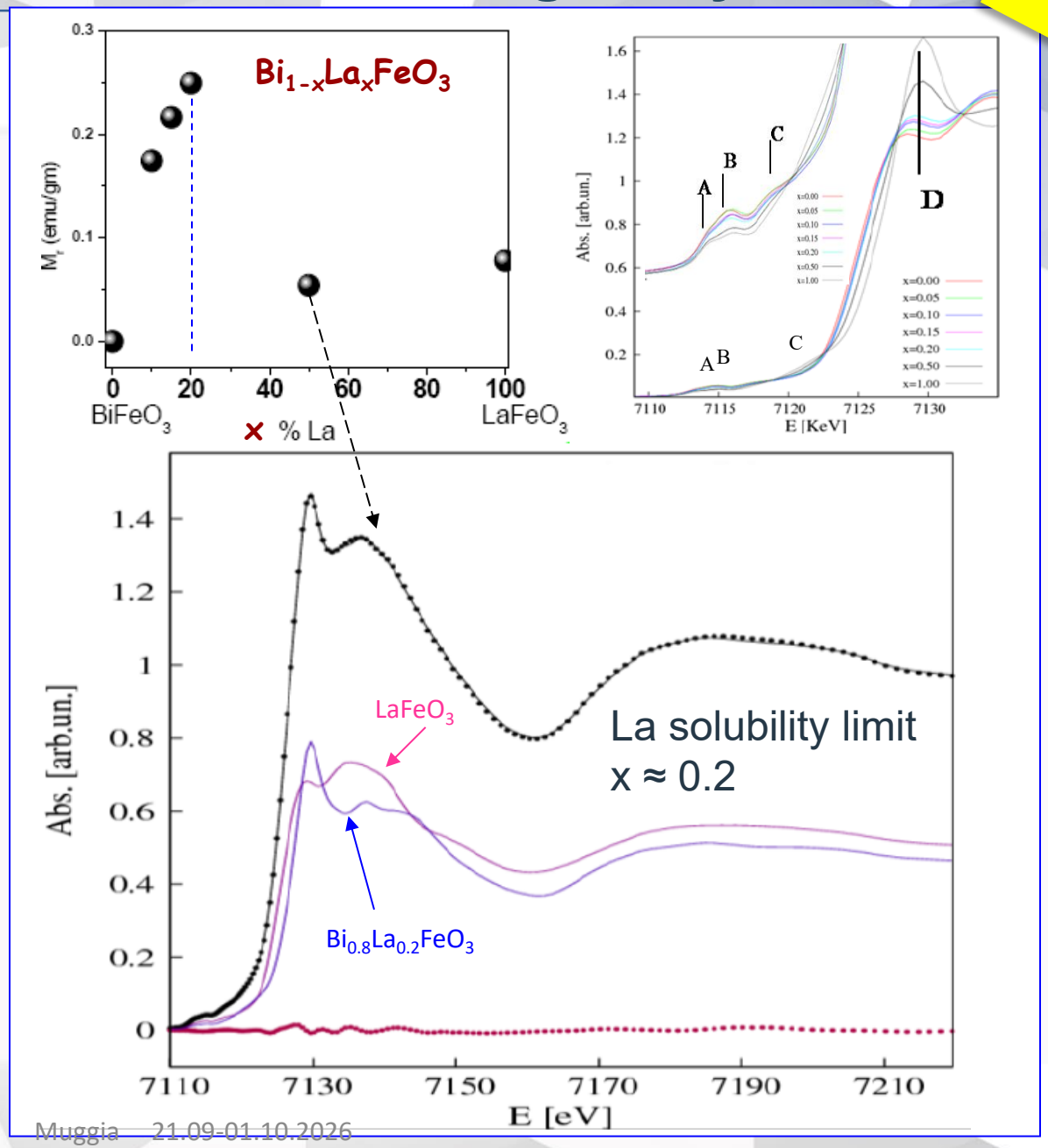
$$\mu^{th} = \sum_j \alpha_j \mu^{ref_j}$$

$$R^2 = \sum_i \left(\mu^{exp}(E_i) - \mu^{th}(E_i)\right)^2$$



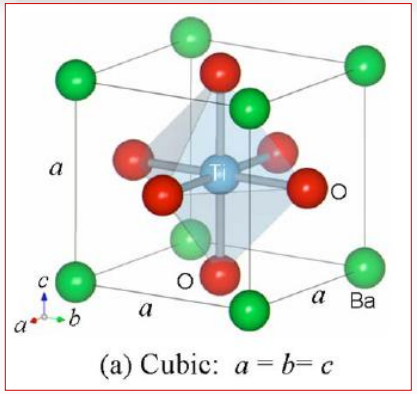


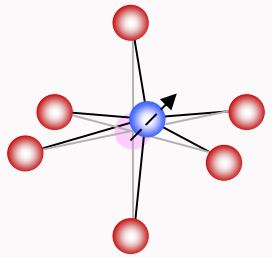
Deepti Kothari *et al* 2010 *J. Phys.: Condens. Matter* **22** 356001



Fe-doped $BaTiO_3$: dilute magnetic ions?

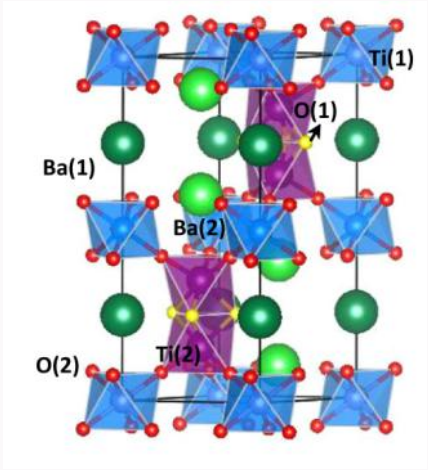
$BaTiO_3$





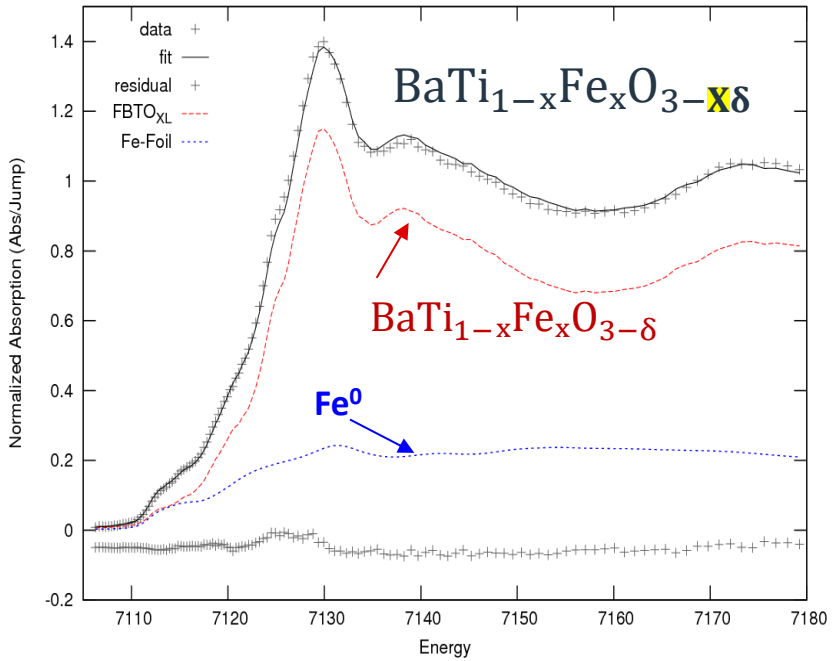
Ti^{4+} off-centering creates local dipoles. Their collective ordering produces ferroelectricity in $BaTiO_3$.

$BaTi_{1-x}Fe_xO_{3-\delta}$



Oxygen deficiency + Fe doping adds magnetic functionality and may stabilize the ferroelectric phase.

Strong oxygen deficiency **Xδ** can give Fe^0 segregation. This local chemical heterogeneity complicates the interpretation of magnetoelectric behaviour.

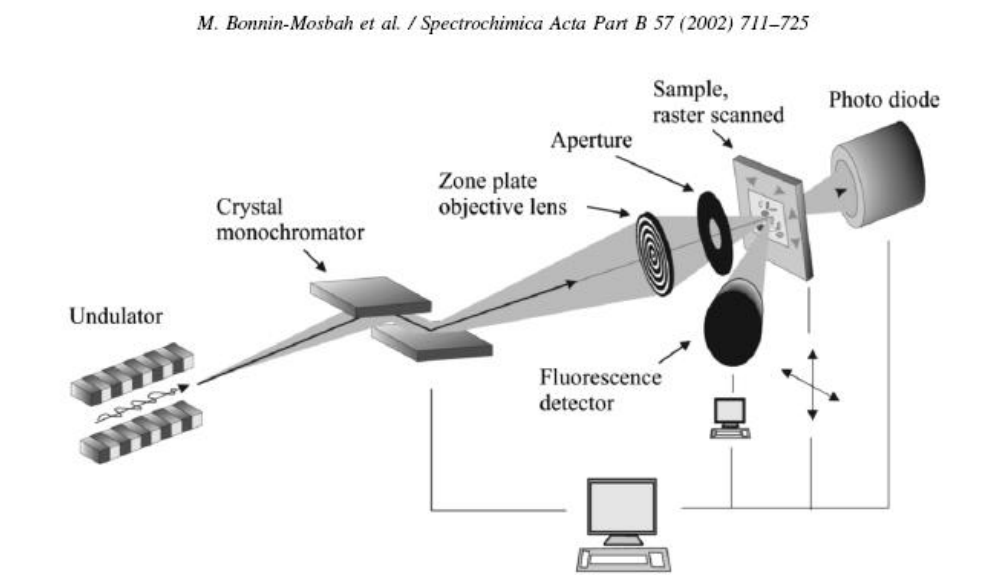


1% of metallic Fe fraction (likely poorly crystalline) escape detection by conventional XRD.

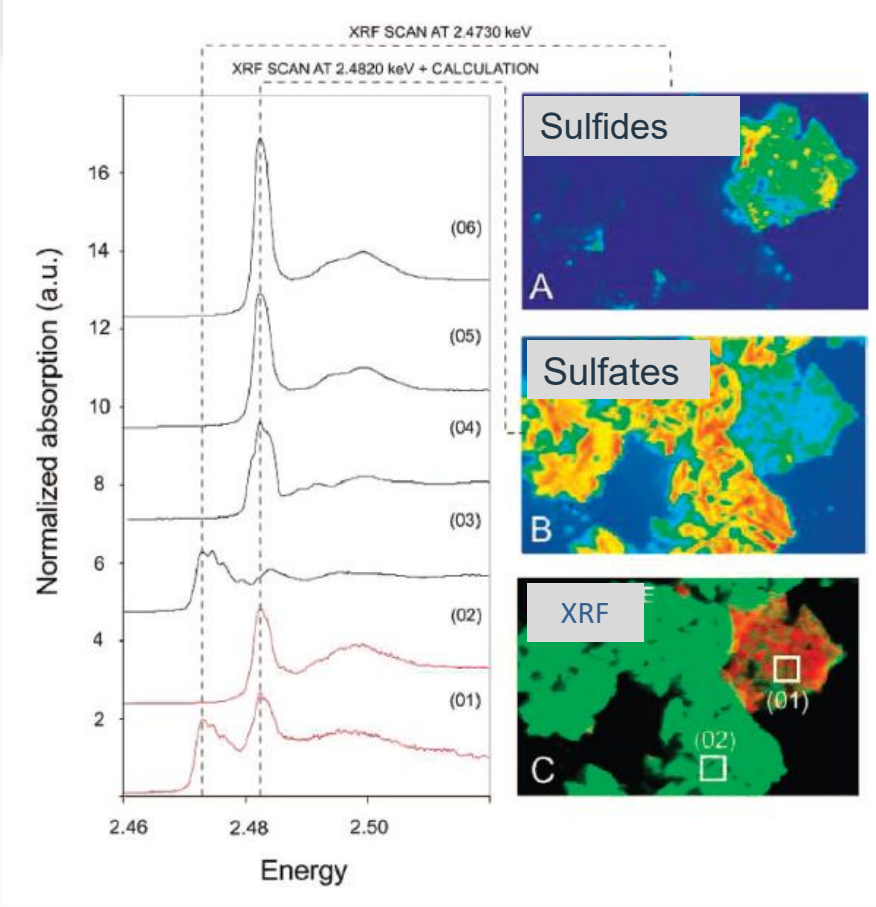
T. Chakraborty, C. Meneghini, G. Aquilanti, S. Ray, J. Phys.: Condens. Matter 25 (2013) 23600
T. Chakraborty, C. Meneghini, G. Aquilanti, S. Ray, Advanced Functional Materials (2014)

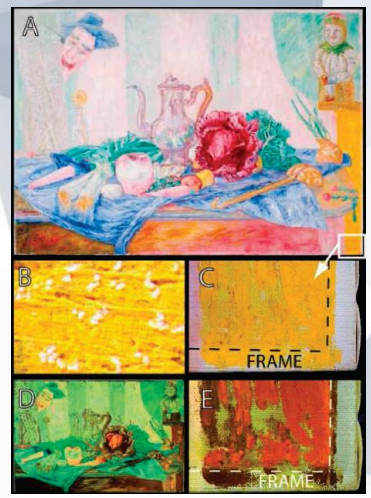
2D XRF and micro-XANES mapping

XANES maps chemical species



Hyperspectral maps distinguish chemical species that an elemental map alone cannot separate.



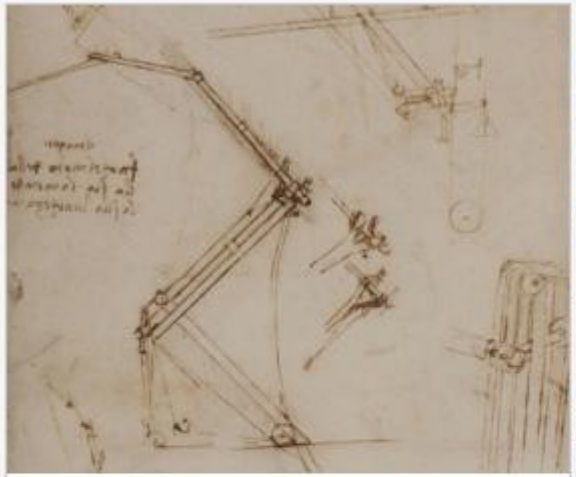


Light-induced modifications of yellow CdS pigments can produce white regions.
Micro-XANES maps the chemical transformations associated with colour changes

(01) yellow paint in sample, (02) white/transparent globules in sample, (03) CdS, (04) anglesite ($PbSO_4$), (05) $CdSO_4$, (06) $CdSO_4 \cdot H_2O$.

ESRF microprobes: examples in cultural heritage and biomedical specimens

Cultural heritage

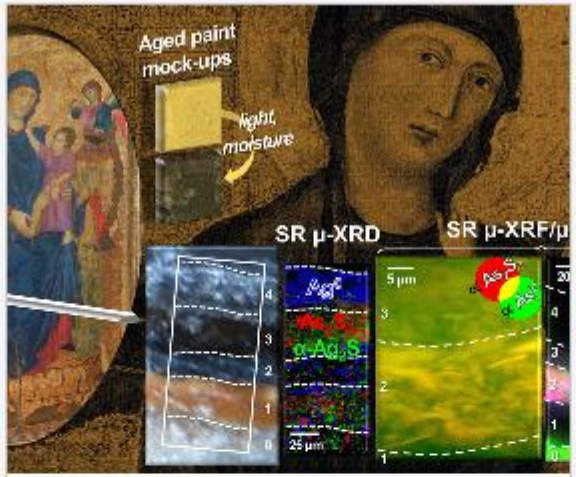


13-06-2023

Revealing new insights into black stains on the passepartout of Leonardo da Vinci's Codex Atlanticus

→ *Read more*

Link.html

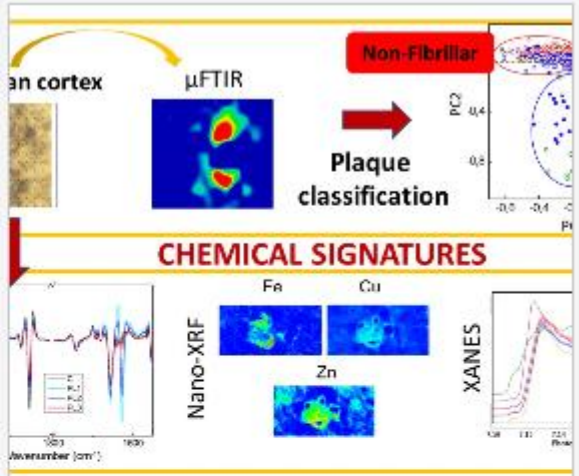


16-12-2021

Revealing the causes of darkening of "fake-gold" decorations on medieval paintings

→ *Read more*

Link.html



14-06-2021

Characterising amyloid plaques in Alzheimer's disease

→ *Read more*

Link.html

Bioremediation: organisms influence pollutant mobility

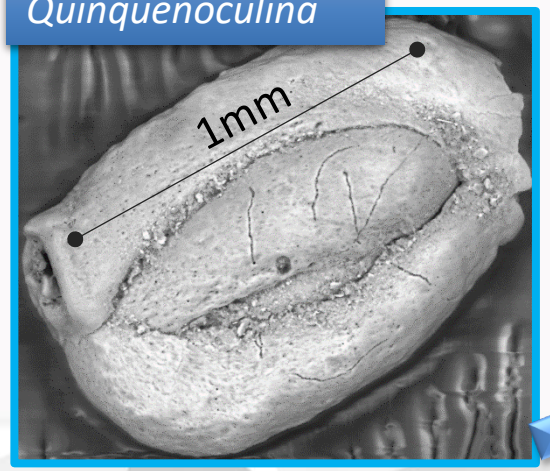
Bio/Geo sciences

XAFS on the bulk

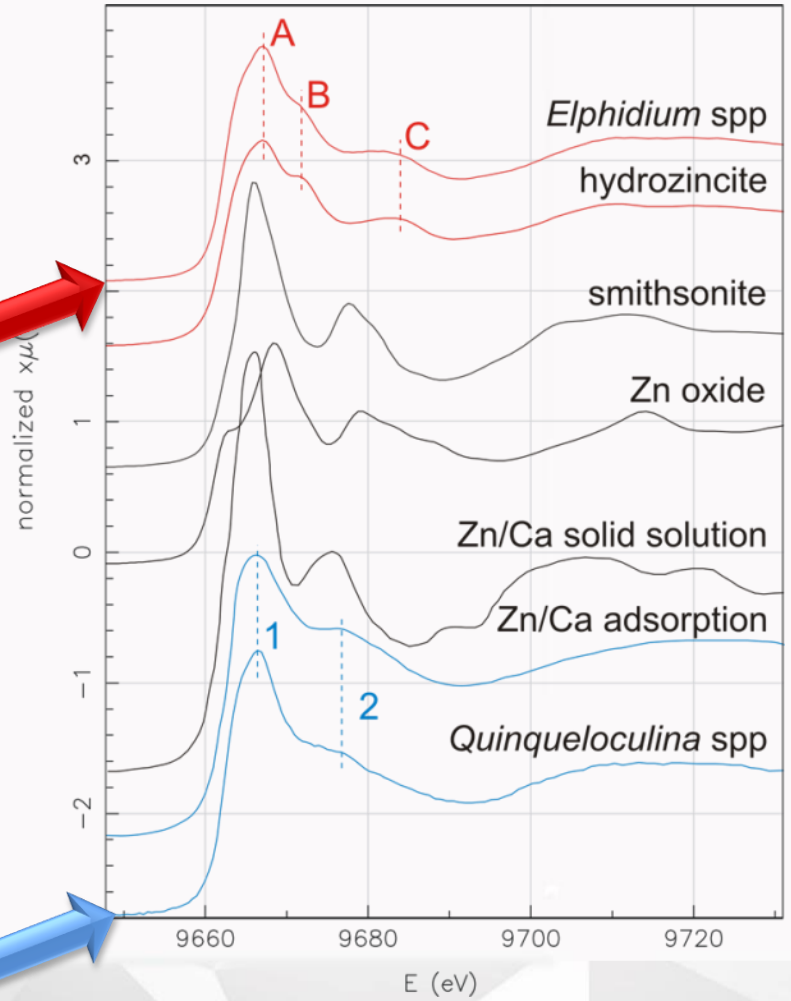
XRF maps

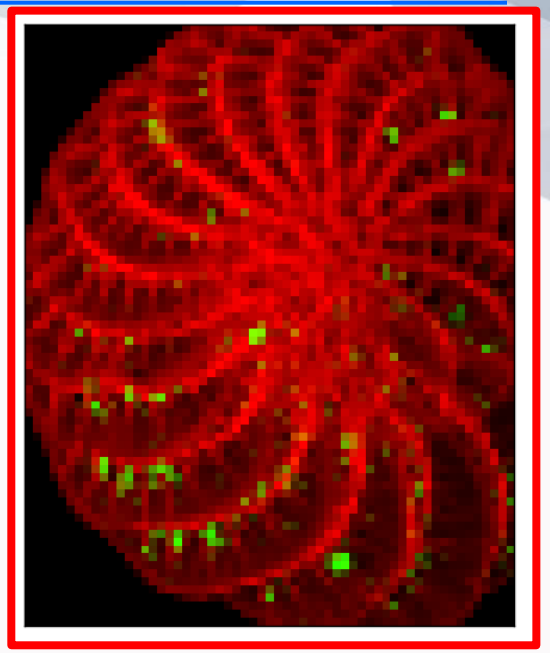
Elphidium

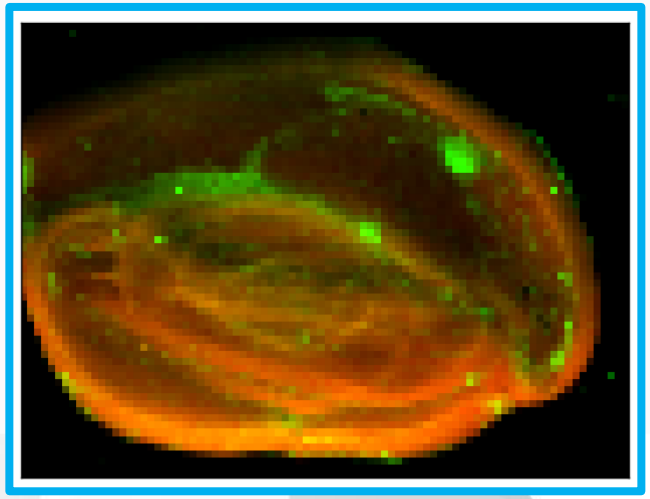
Quinquenoculina



XANES



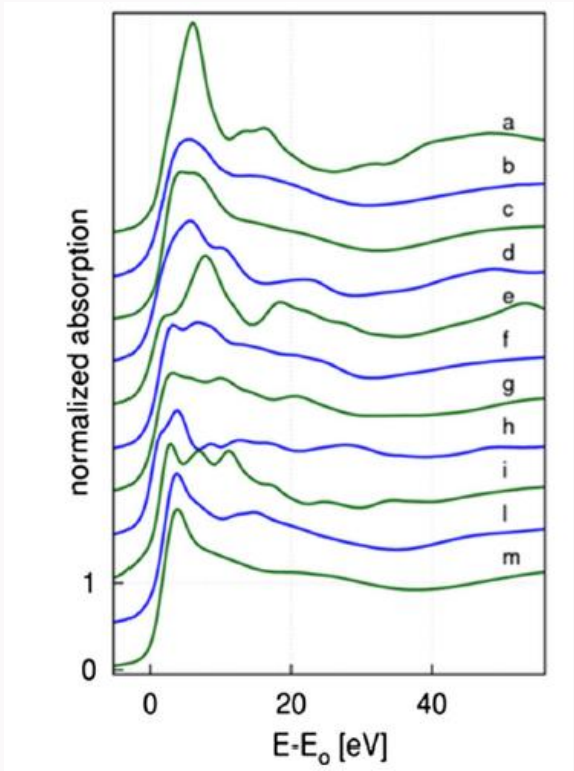


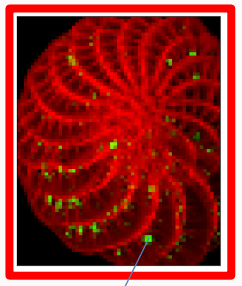


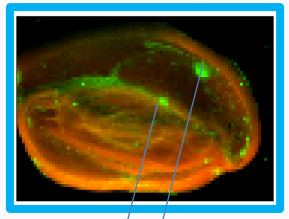
Zn

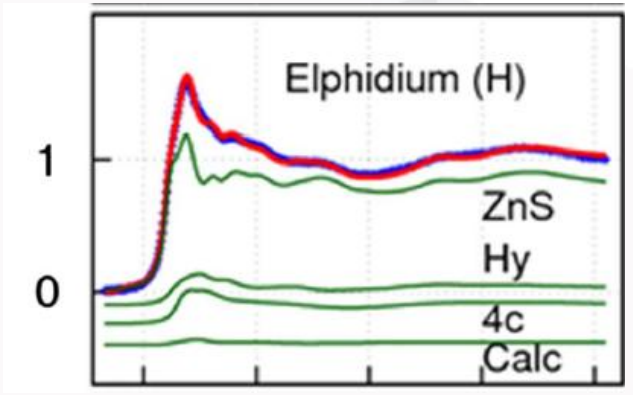
Chemical Geology 477 (2018) 100–111

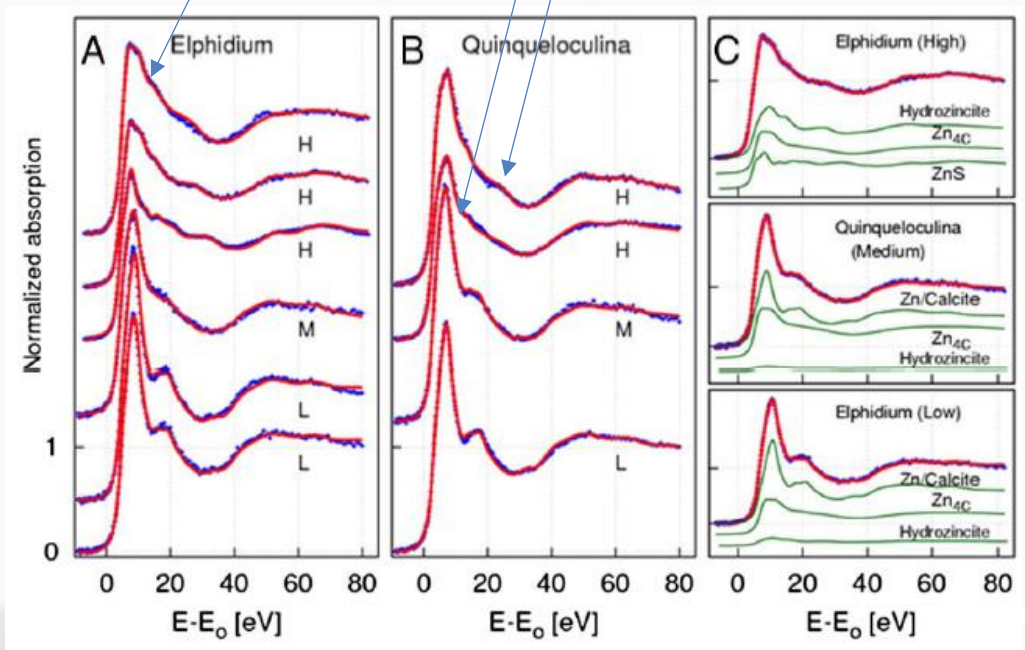
Bioremediation: identifying the local environment of Zn

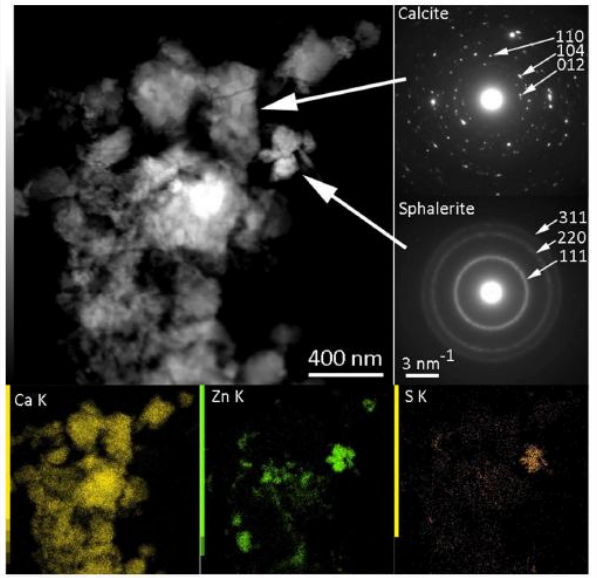








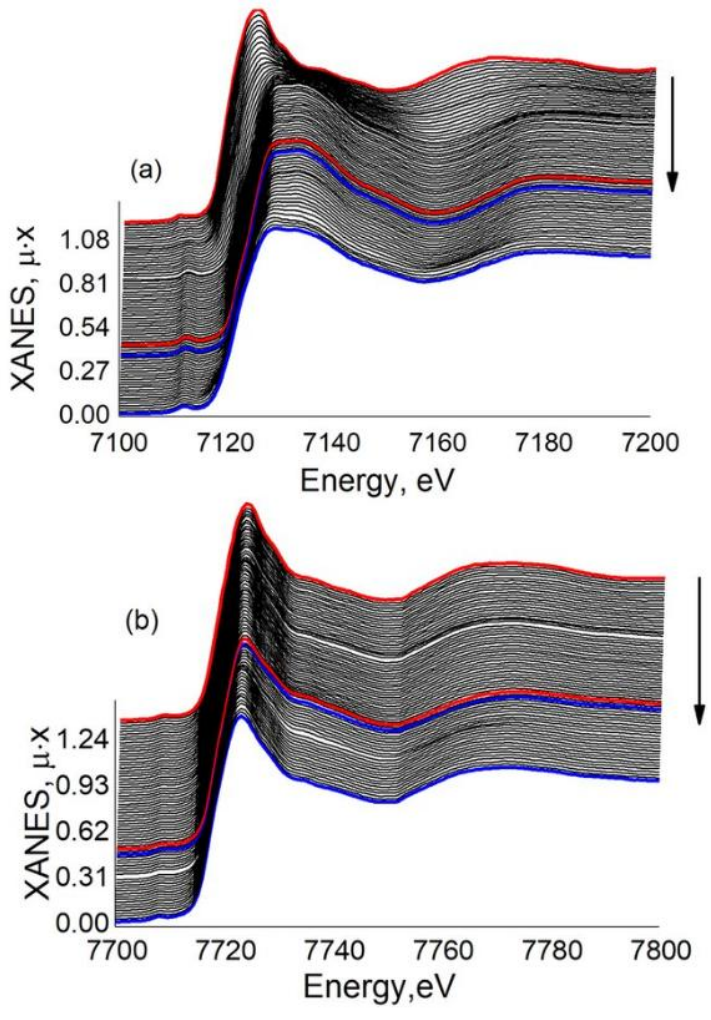




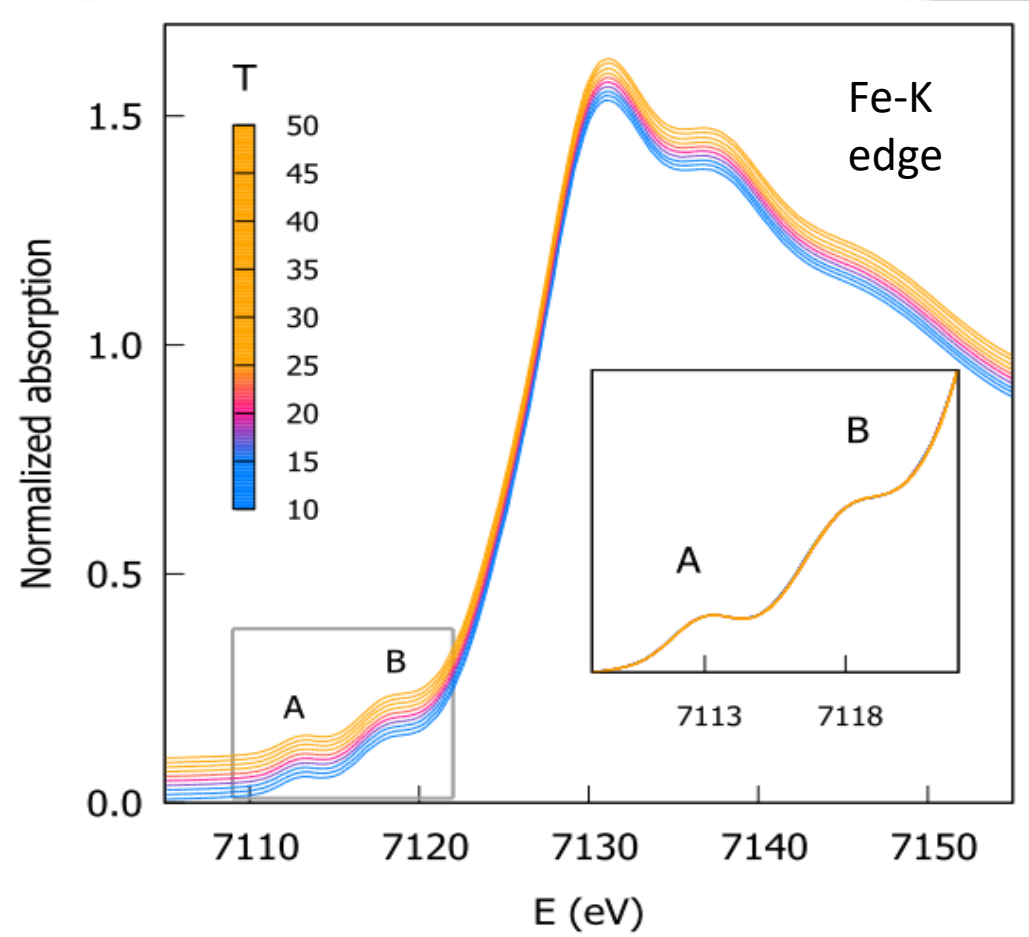
G. De Giudici, D. Medas, P. Lattanzi, C. Meneghini et al. Work in preparation

Large XANES datasets and subtle spectral changes

Fast acquisition
produces large (huge) datasets



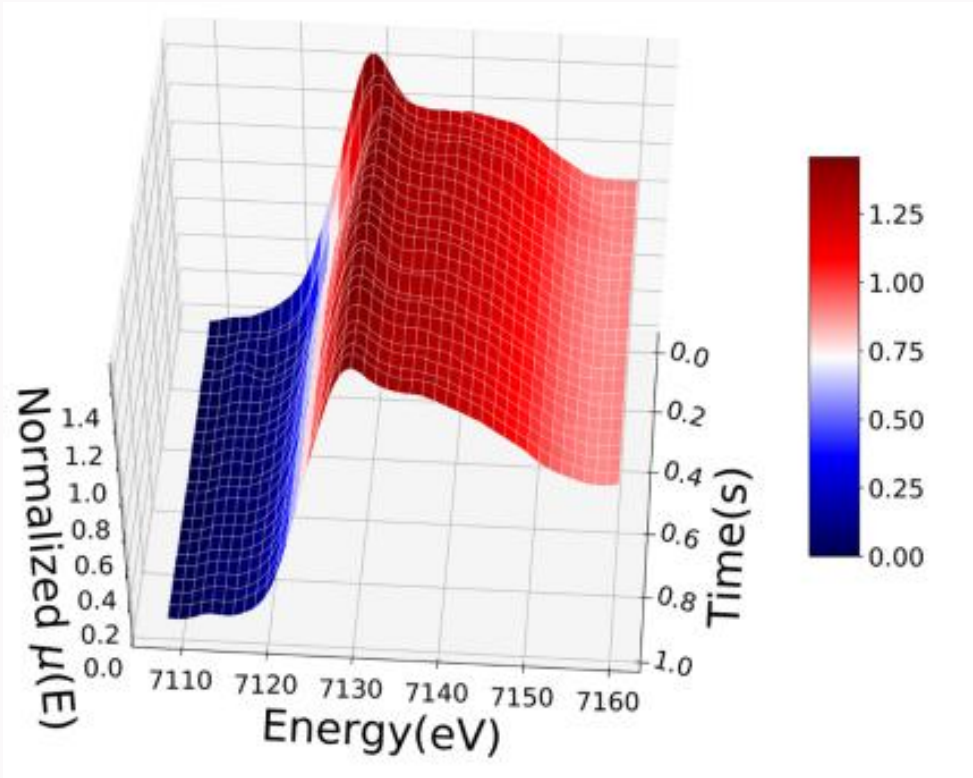
High-quality data
reveal tiny spectral variations



Time-resolved XANES of a chemical reaction

large datasets require Multivariate methods: PCA, t-SNE, Cluster analysis….

Chemistry



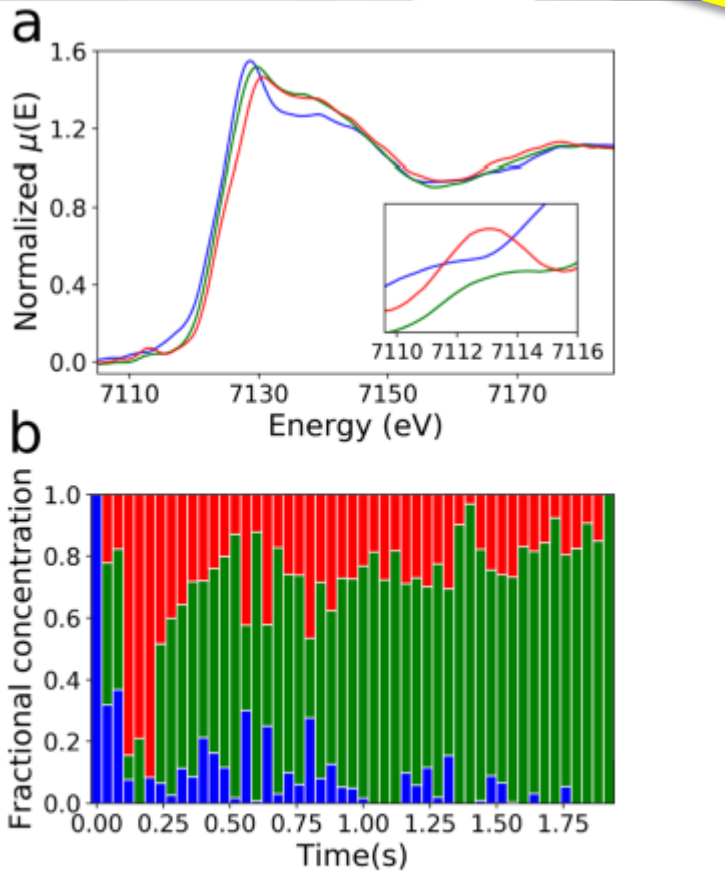


Figure 4. Fe K-edge XANES spectra (a) and fractional concentration profiles (b) extracted by using the transformation matrix-based decomposition.

Inorg. Chem. 2020, 59, 9979 – 9989

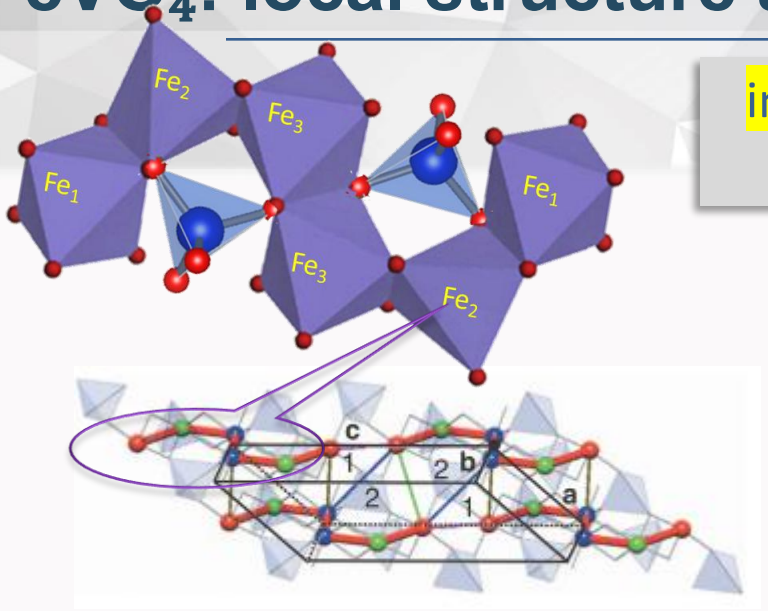
Direct Mechanistic Evidence for a Nonheme Complex Reaction through a Multivariate XAS Analysis

Francesco Tavani,* Andrea Martini, Giorgio Capocasa, Stefano Di Stefano, Osvaldo Lanzalunga, and Paola D'Angelo*

DOI: 10.1021/acs.inorgchem.0c01132

$FeVO_4$: local structure and multiferroicity

Fundamental material science



interplay between **spin frustration**, **magnetoelectric** coupling, and **magnetocaloric** effects.

Type-II multiferroic with **non-collinear magnetism** inducing **ferroelectric polarization**. Two antiferromagnetic transitions. Complexphase diagram and **large magnetocaloric** response

How local structural changes are related to magnetic and ferroelectric order?

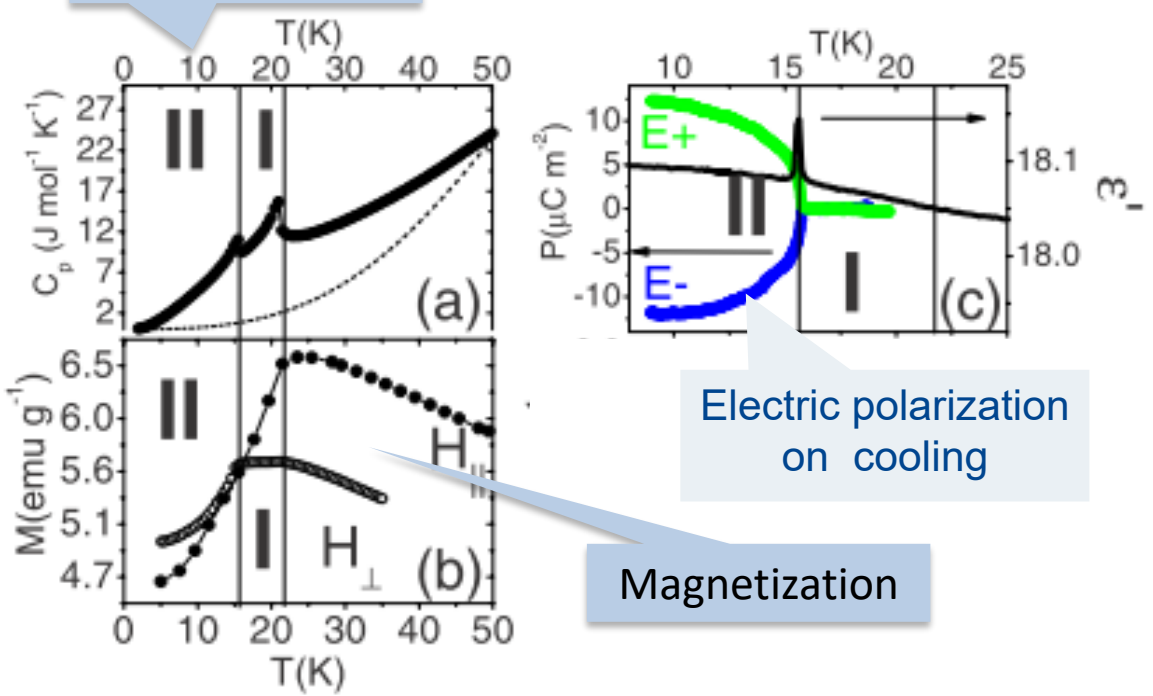
PHYSICAL REVIEW B **80**, 220402(R) (2009)

Multiferroicity and spiral magnetism in $FeVO_4$ with quenched Fe orbital moments

A. Daoud-Aladine,[1,*] B. Kundys,[2] C. Martin,[2] P. G. Radaelli,[1,3] P. J. Brown,[4] C. Simon,[2] and L. C. Chapon[1]

Heat capacity

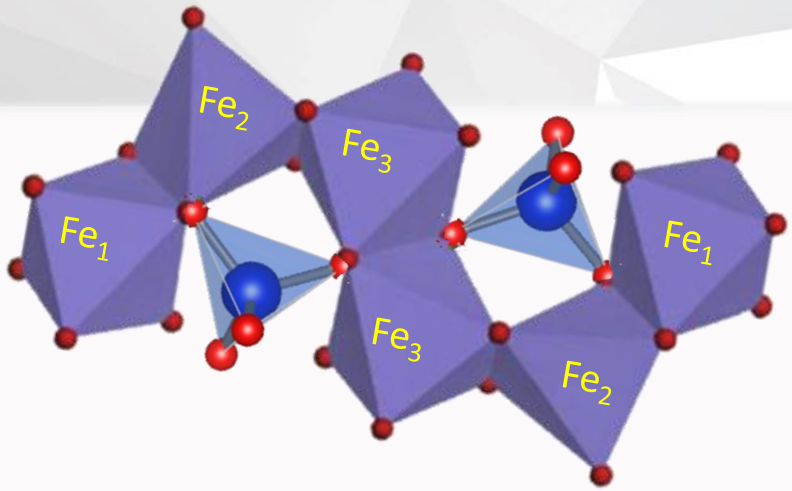
Magnetic transitions at 22 K and 15 K
Ferroelectric ordering below 15 K



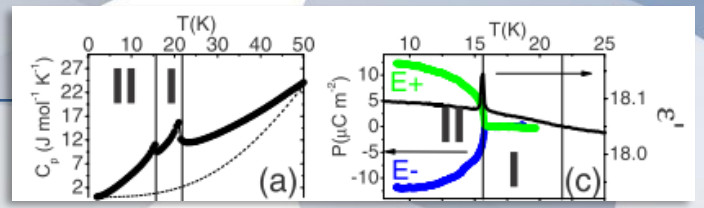
Electric polarization on cooling

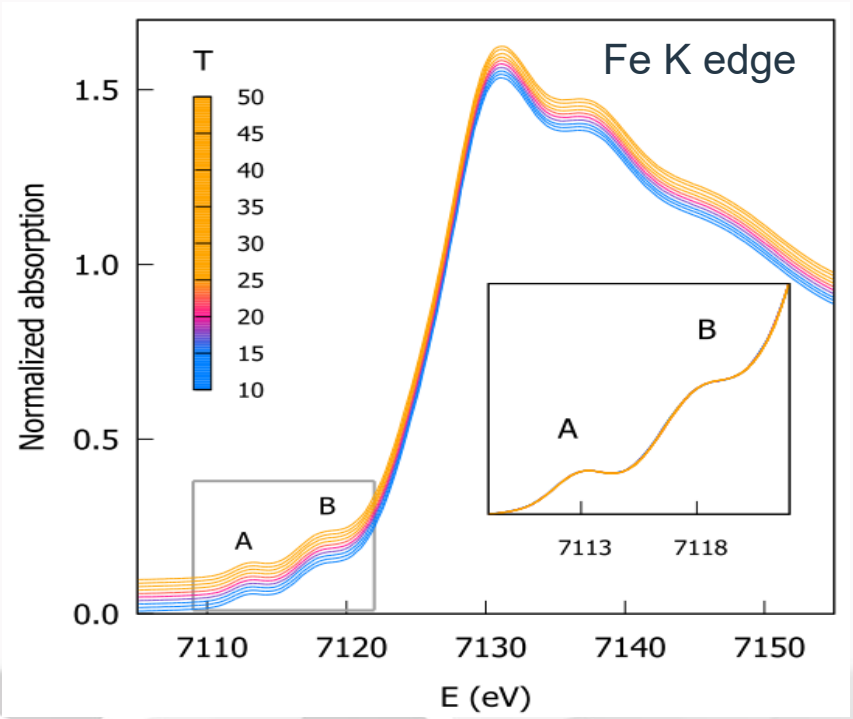
Magnetization

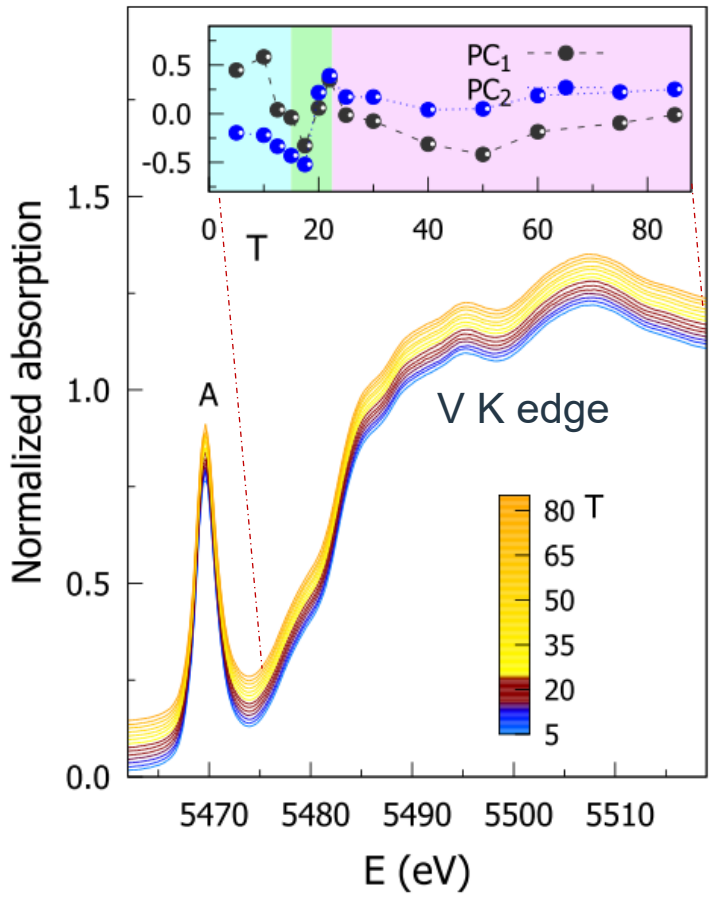
$FeVO_4$: temperature-dependent XANES

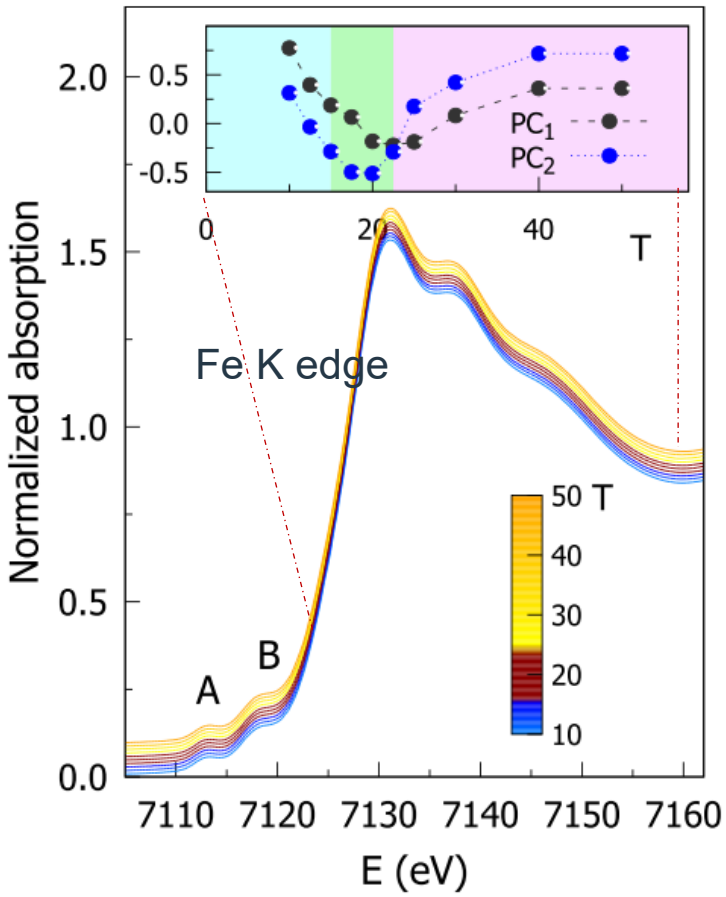


Multivariate Analysis reveals tiny *spectral changes* associated to magnetic transitions $\simeq 20\ K$.

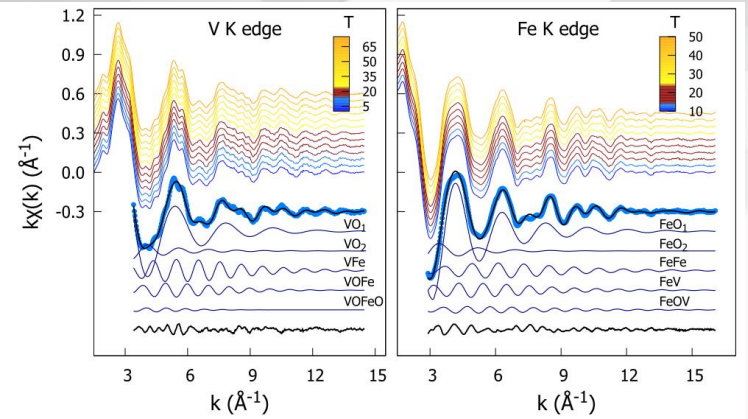


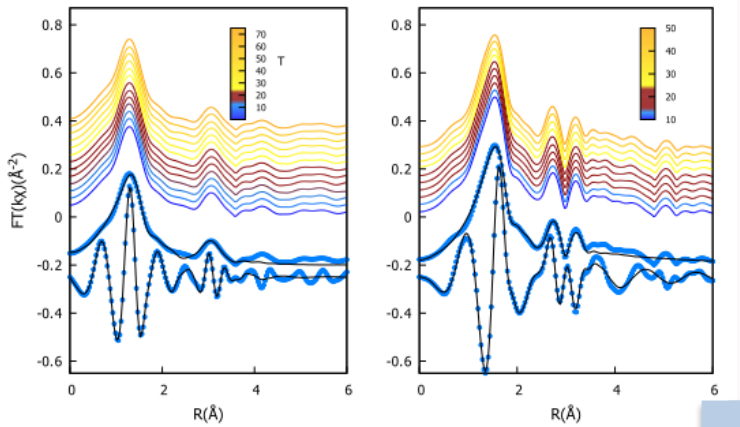


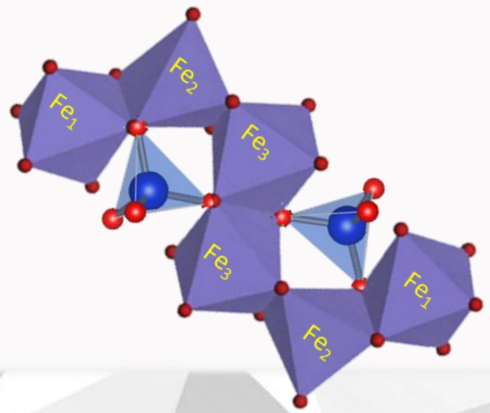




$FeVO_4$: structural changes along exchange pathways



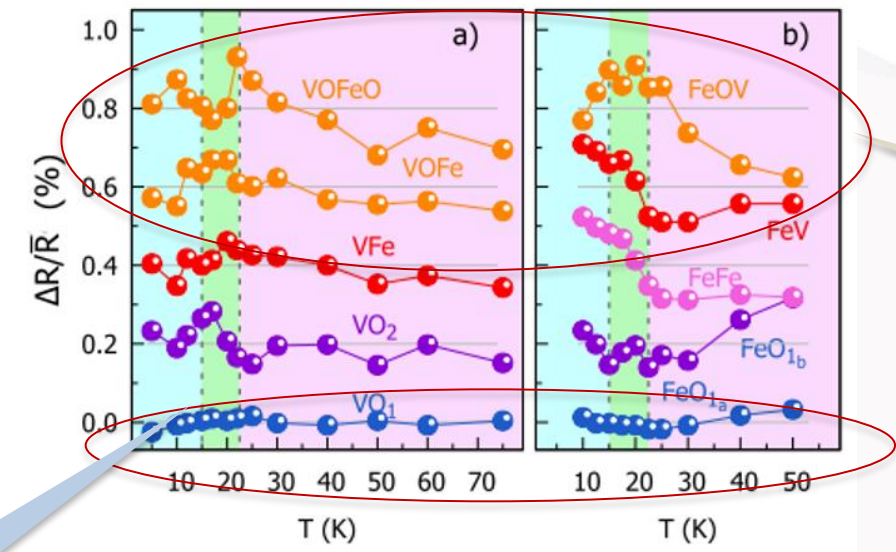


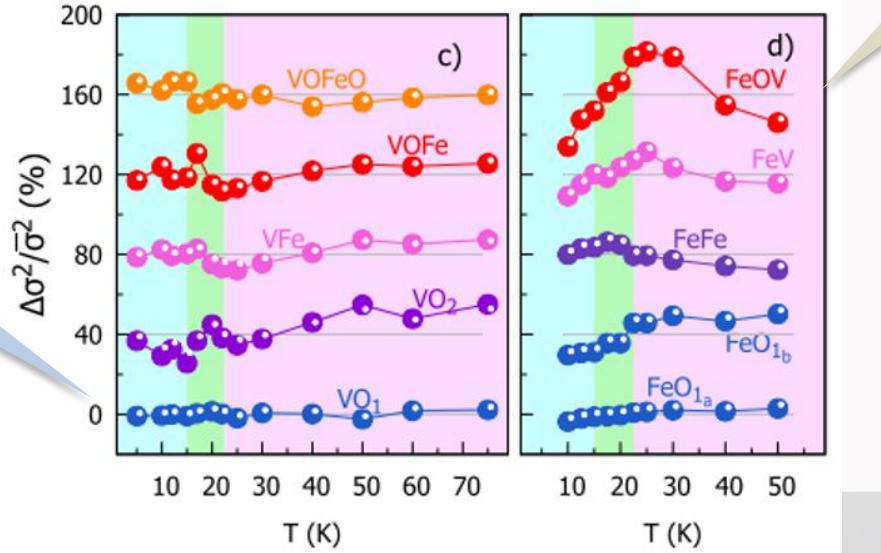


No resolved changes within FeO_6 or VO_4 units

V K-edge

Fe-K edge



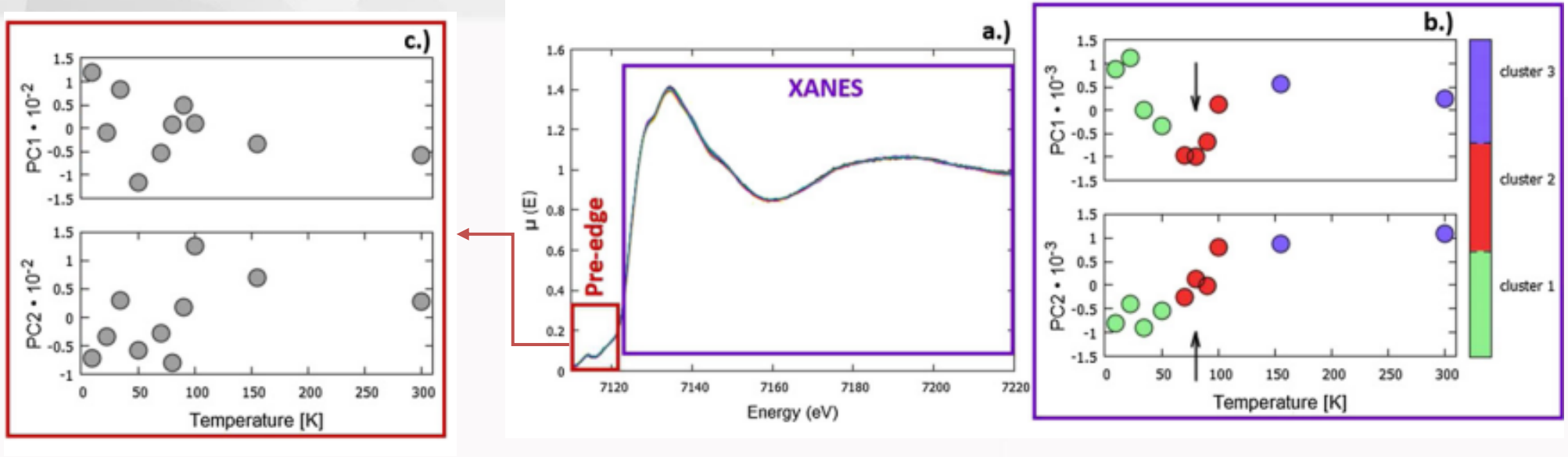


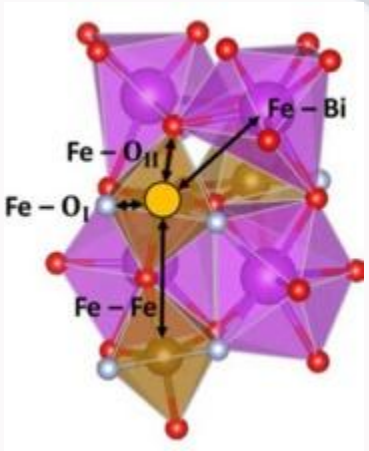
Changes in $FeO_6 - VO_4$ $FeO_6 - FeO_6$ connectivities

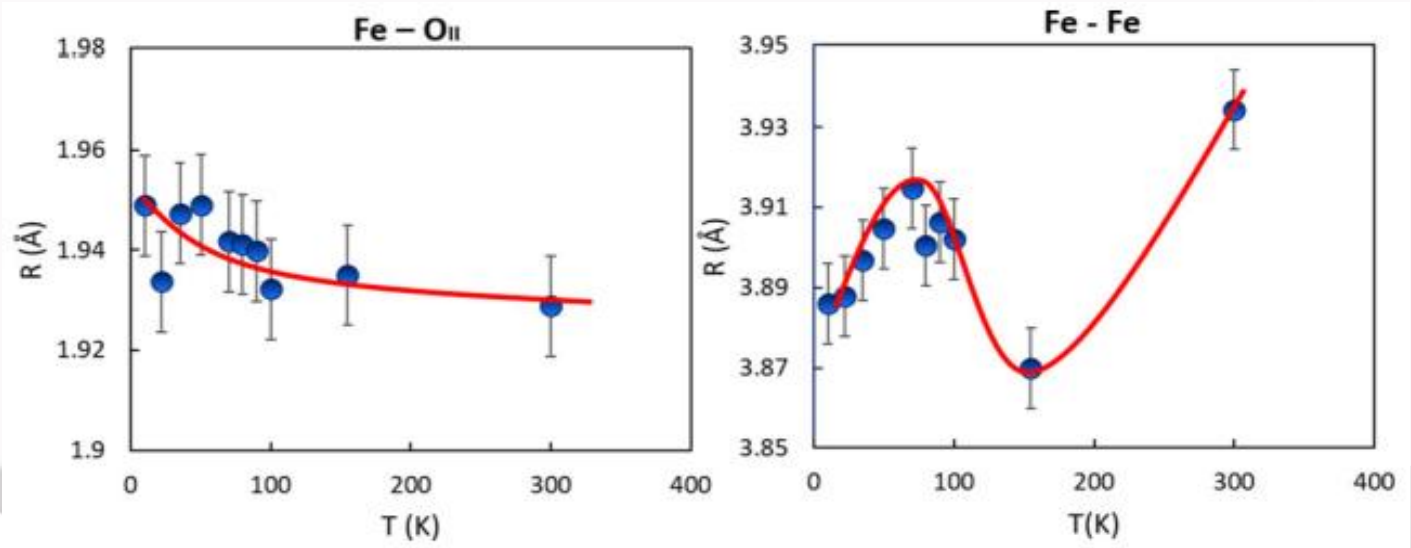
$Bi_5FeTi_3O_{15}$ ceramics: medium-range order and ferroelectricity

PCA/k-mean: **pre-edge**

PCA/K-mean: **XANES**





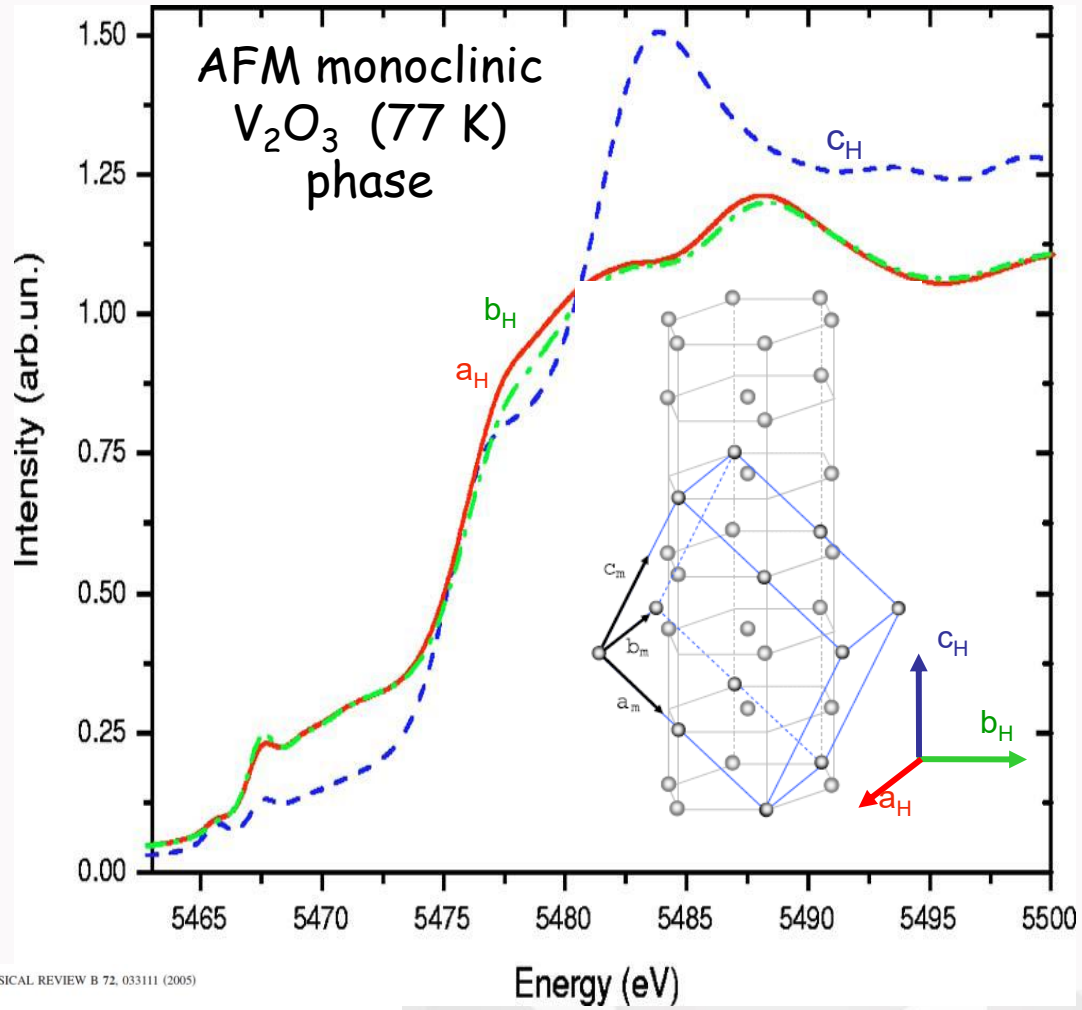


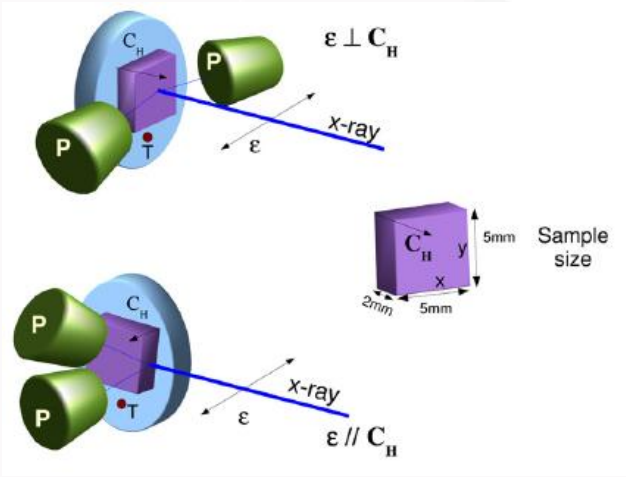
J. Phys.: Condens. Matter **0** (2021) 000000 (11pp) https://doi.org/10.1088/1361-648X/ac0c3b

Lattice assisted dielectric relaxation in four-layer Aurivillius $Bi_5FeTi_3O_{15}$ ceramic at low temperatures

Deepak Prajapat[1], Akash Surampalli[1], Irene Schiesaro[2], S D Kaushik[3], Carlo Meneghini[2], Archna Sagdeo[4,5], V G Sathe[1], V Siruguri[3], Edmund Welter[6] and V Raghavendra Reddy[1]

Polarized XANES: directional probe for not isotropic structures





Structural dichroism (absent in hexagonal HT phase) is the fingerprint of monoclinic distortion

PHYSICAL REVIEW B 72, 033111 (2005)

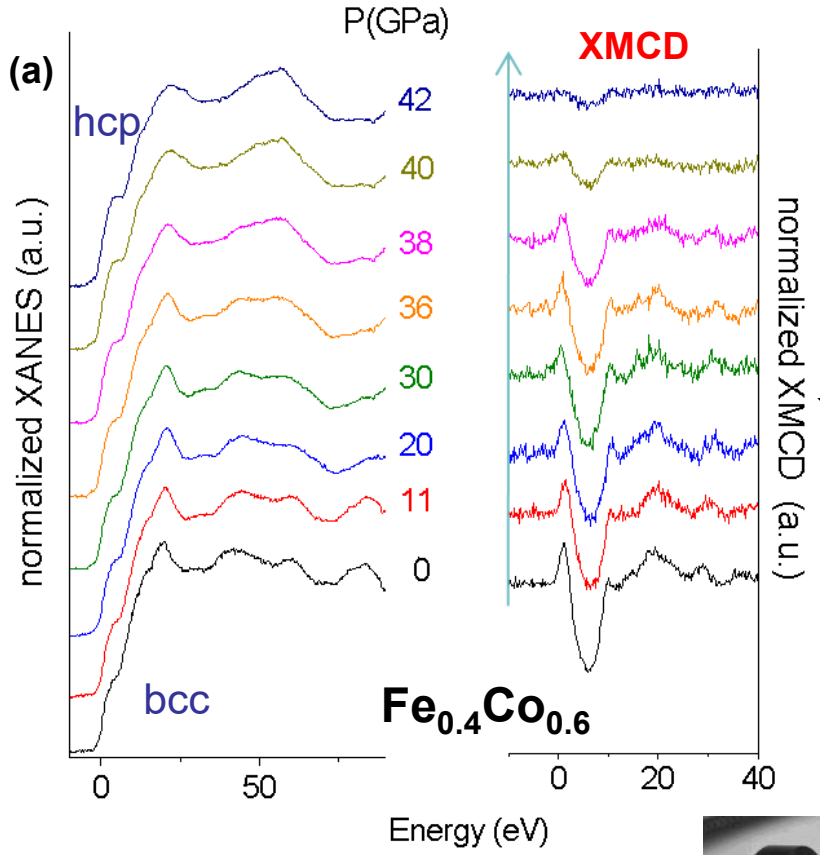
Structural dichroism in the antiferromagnetic insulating phase of V_2O_3

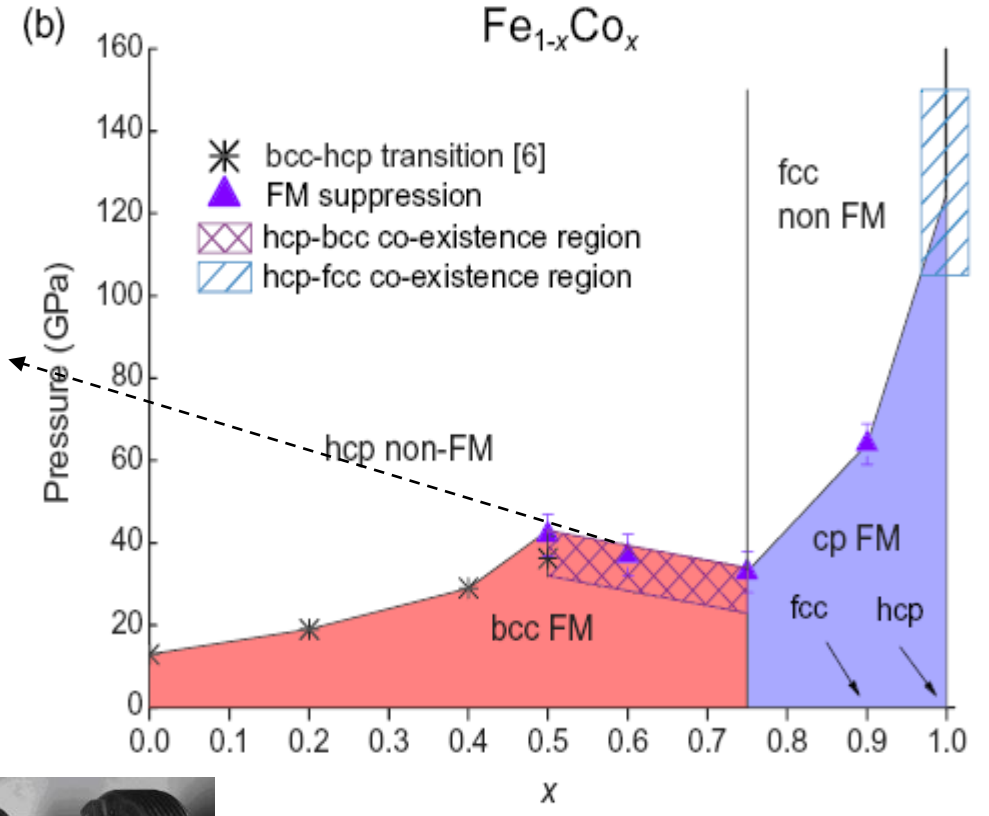
C. Meneghini,[1] S. Di Matteo,[1,2] C. Monesi,[1] T. Neisius,[3] L. Paolasini,[3] S. Mobilio,[1,2] C. R. Natoli,[2] P. A. Metcalf,[4]

XANES-XMCD under extreme condition studies

High pressure structural and magnetic diagram of phase of 3d metal alloys

XANES





R. Torchio et al. High Pressure Research 31, 148-152 (2011)

Thank you for your attention

Carlo Meneghini

carlo.meneghini@uniroma3.it