Phenomenological approach to XANES data analysis:

Shortcuts to understand local structure and chemistry from XANES spectra

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http://host.uniroma3.it/docenti/meneghini/index.html

XIV School on Synchrotron Radiation:
Fundamentals, Methods and Applications
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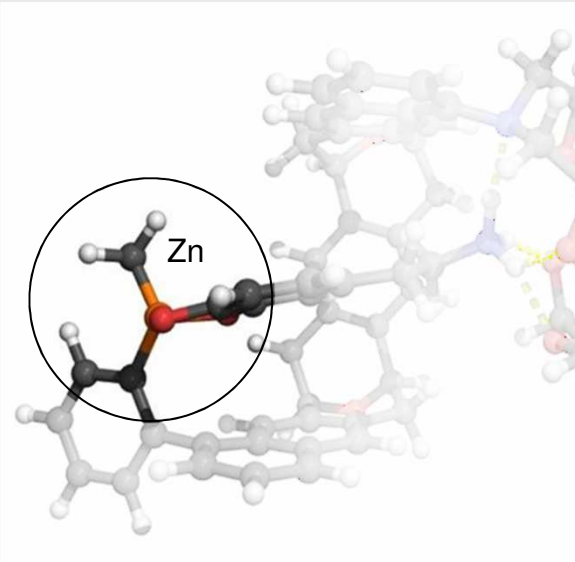
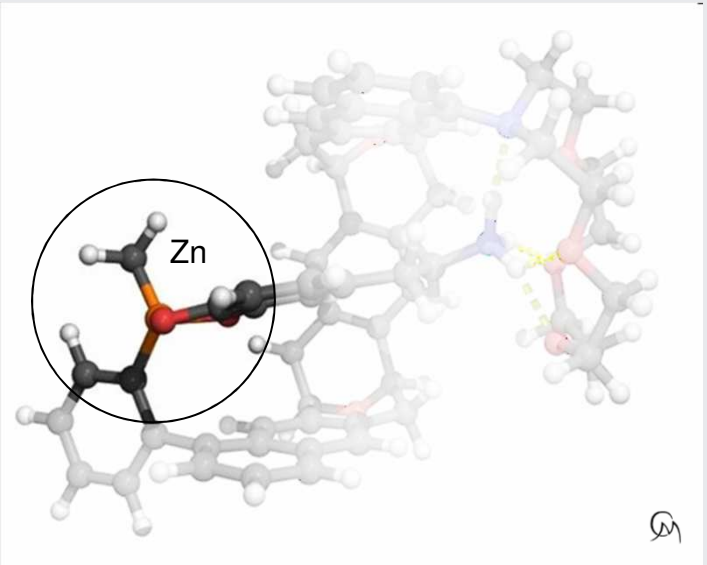
XAFS is a local sensitive, chemical selective probe which may provide structural, electronic and even magnetic (XMCD) details

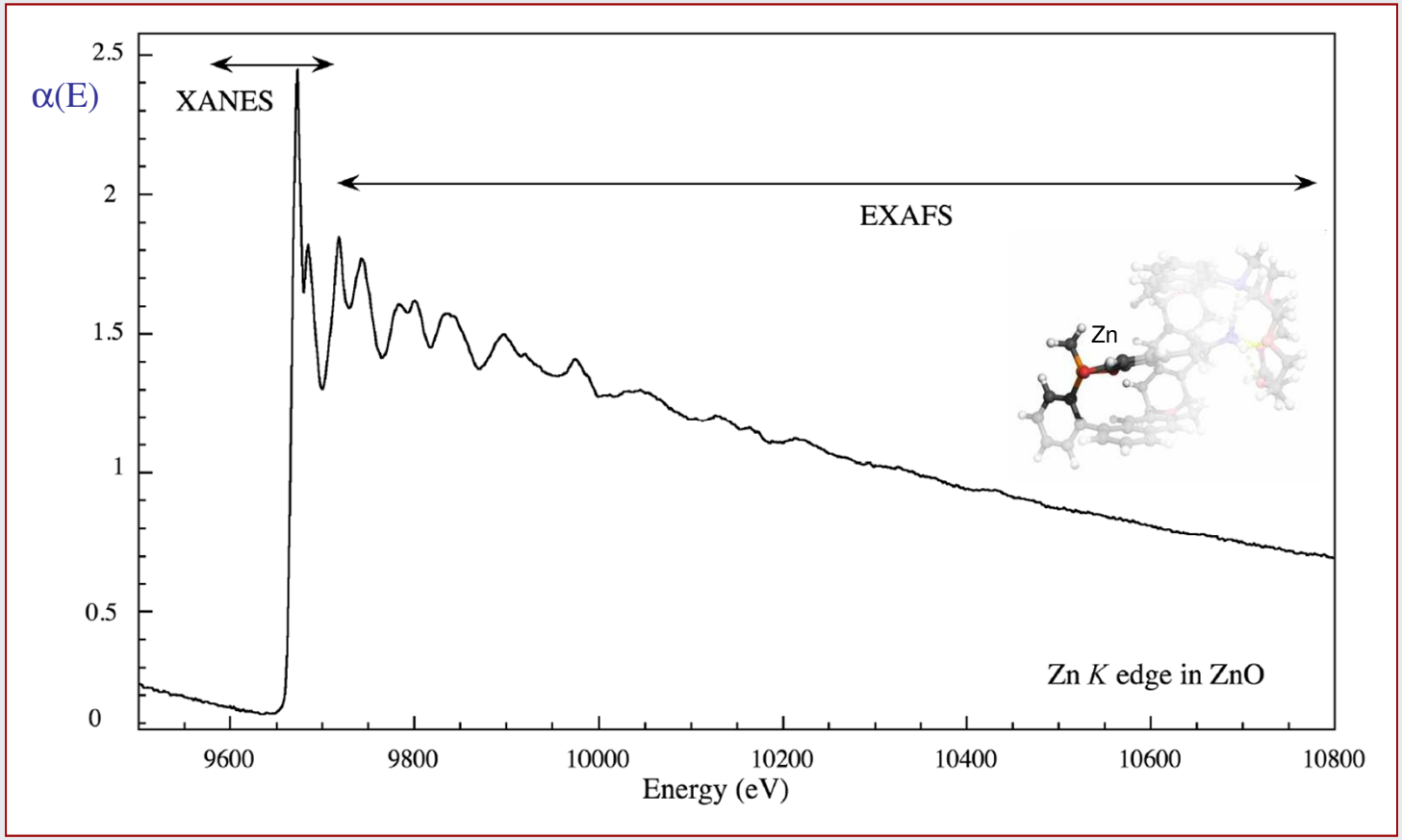


Subjective (Absorber) view of the local atomic structure in your sample

XAFS is a local sensitive, chemical selective probe which may provide structural, electronic and even magnetic (XMCD) details

- Applicable to materials in any aggregation state: gas, liquid, solid, single crystals, powders, amorphous, nanostructures, etc....
- Measurable from bulk to the highest diluted samples (micro-molar)
- Versatile probe (bulk, surfaces, layered structures, quantum structures, etc...)
- Simple experimental set-up and easy data collection
- Fast (quick XAFS) and ultrafast (dispersive) data collection
- Directional sensitivity (polarized XAS): to probe structural anisotropy
- Element selective Magnetic state sensitive (XMCD)





EXAFS region: simple analytical formula suited for data fitting and *easy* structural refinement

$$\chi(k) = \frac{1}{k}\sum_j A_j(k, r_j) sin(2kr_j + \psi_j(k))$$

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

XANES region:

Hard theory

lack of an analytical expression

long computation time

Applications of XANES spectroscopy systematically increases

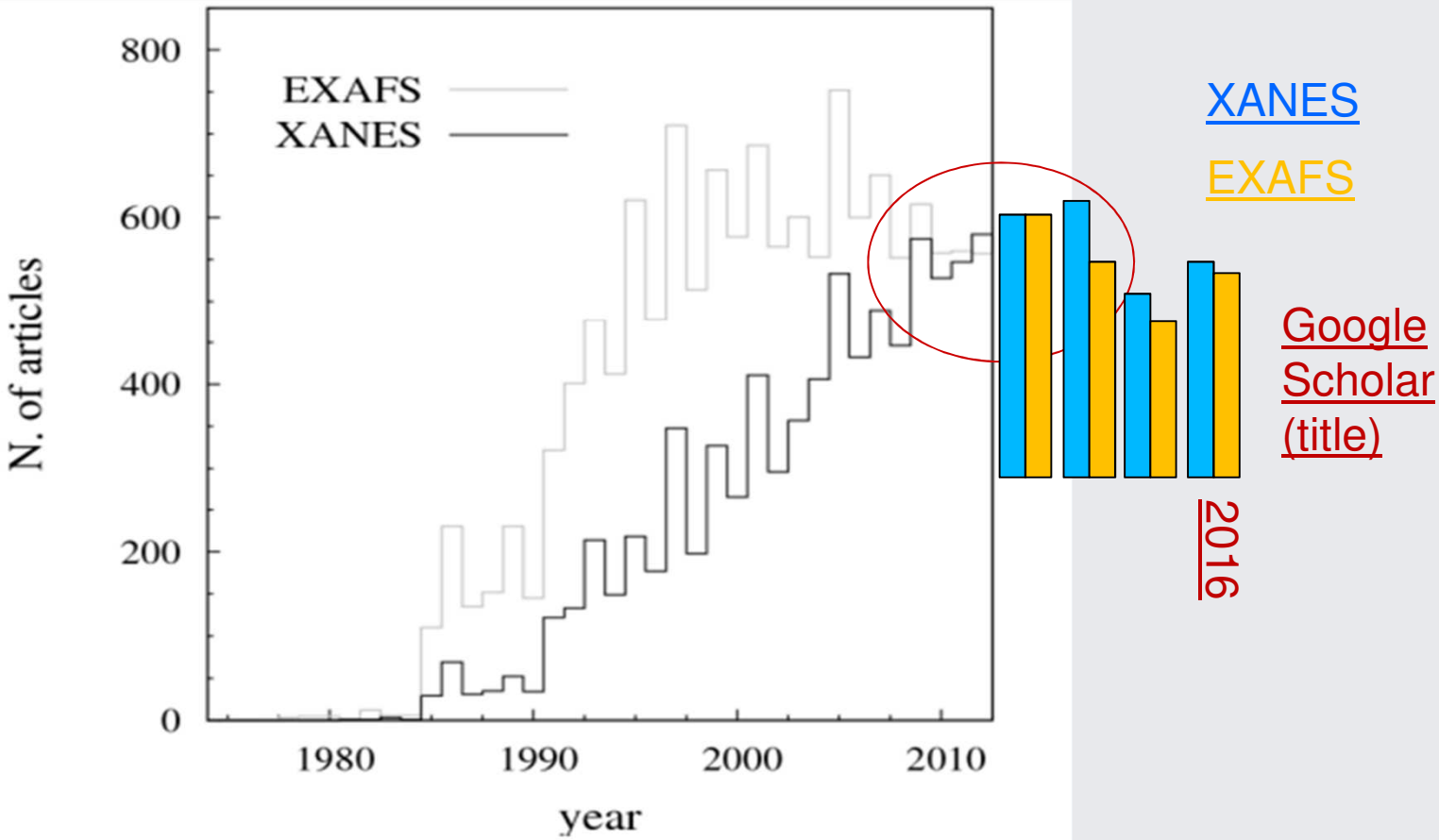


Fig. 1. Results of database search on ISI-web of knowledge using "EXAFS" ("XANES") in *Topic* or *Title* fields.

XANES based probes: valuable advantages

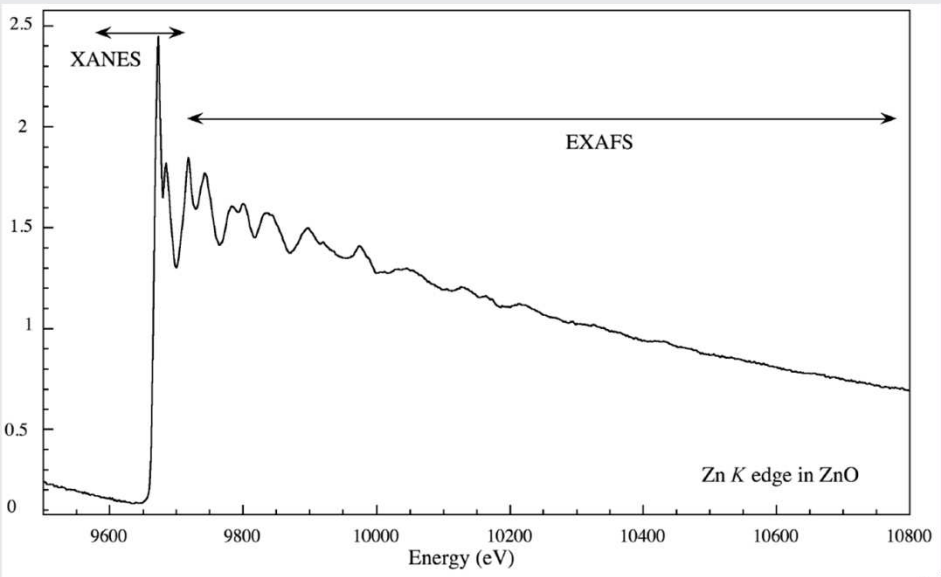
XANES signal is stronger than EXAFS

Damping of XANES signal due to structural disorder is weak

Electronic structure (DoS) and structural topology

Restricted energy range

May provide Chemical selective Magnetic information (XMCD)



XANES signal is dense of electronic, magnetic and structural details

XANES signal is stronger than EXAFS:

- less sensitive to data statistics, sample quality, beam intensity,
- can be measured on less concentrated samples,
- can be measured faster than EXAFS (time resolved experiments),
- can be measured at low energies (i.e. Carbon, Oxygen, Nitrogen K-edges.

XANES theory is complex

Damping of XANES signal due to structural disorder is weak:

- Applications to extreme condition studies: High **T**, High **P**, High **H**....

Electronic structure (DoS) and structural topology:

- XANES features are specially sensitive to the valence state, coordination chemistry, ligand symmetry of the absorber.
- Can be used as fingerprint for chemical speciation in mixtures and inhomogeneous systems.

XANES are prone to simple interpretation for simple and fast (semi-)quantitative analysis

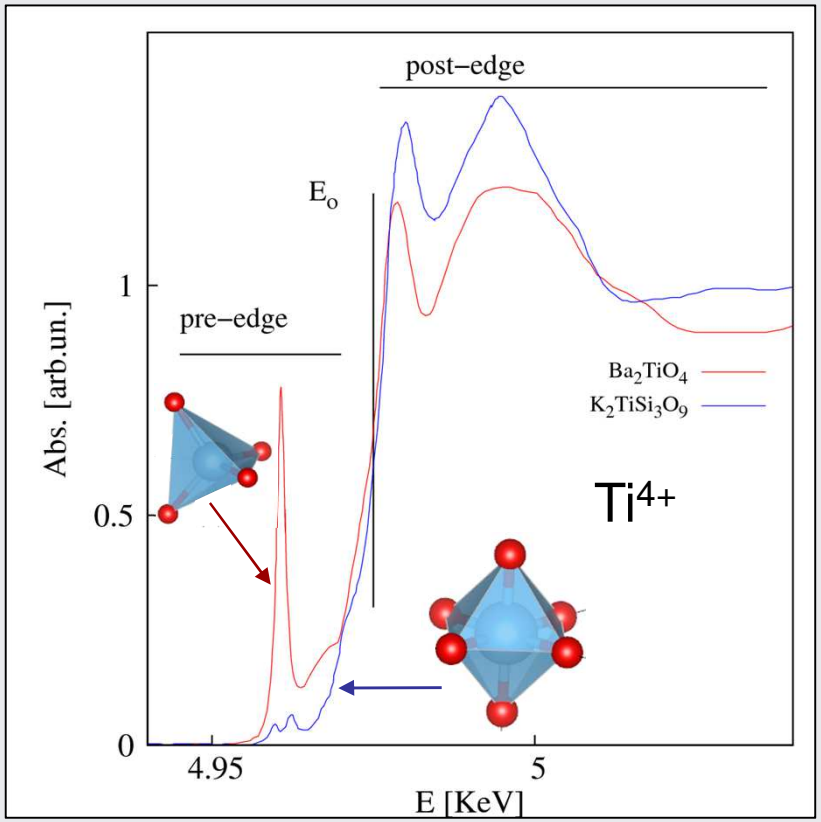
Restricted energy range around the edge:

- Measurements at low energies (i.e. Carbon, Oxygen, Nitrogen K-edges)
- Fast data collection (time resolved XAS)
- XANES Microprobes (mapping) with sub-micrometer resolution

Chemical selective Magnetic information

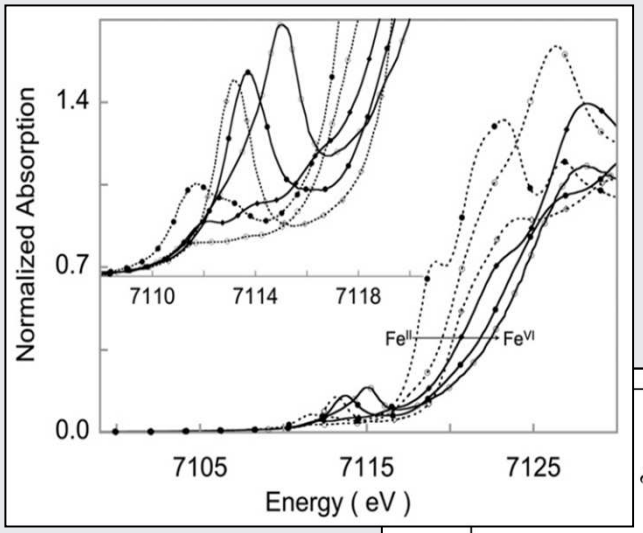
- X ray Magnetic Circular Dichroism (XMCD) signal is an element specific probe for magnetism
- Sum rules at $L_{2,3}$ edges allow distinguishing orbital and spin contributions to the magnetic moment of the photoabsorber

Deeper insight into the XANES region



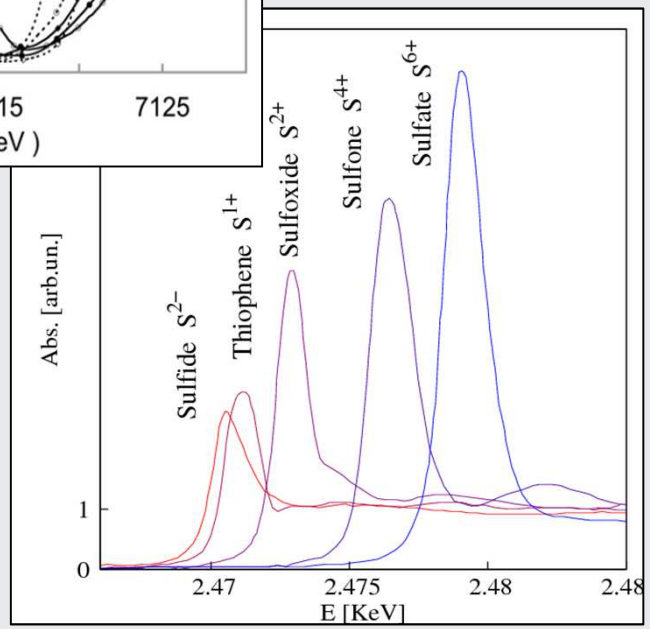
Local symmetry and XANES in Ti^{4+} compounds

XANES features are strongly related to the coordination geometry: coordination number **and** ligand symmetry



Fe K edges: representative XANES Fe in complexes

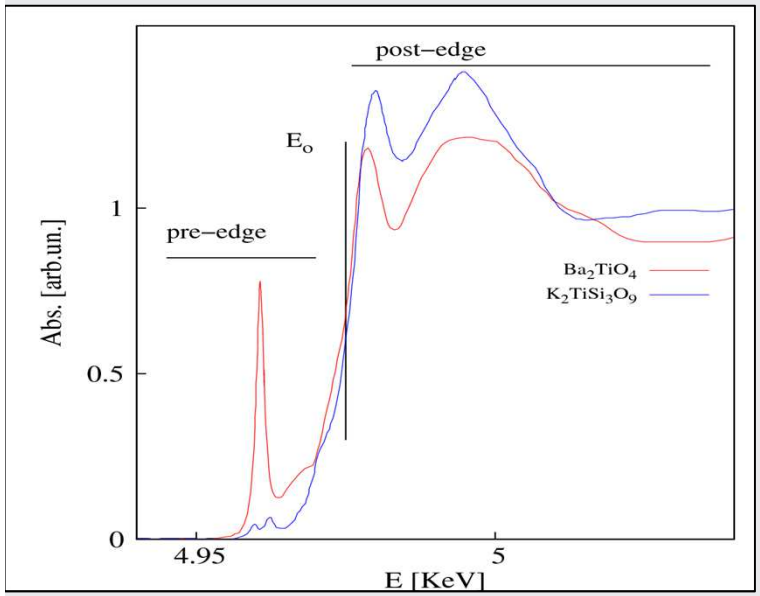
R. Sarangi, Coord. Chem. Rev. **257** 459–472 (2013)



Sulphur K edges: chemical shift as a function of valence state of S-ions

Absorption Edges (energy position and shape) definitively depend on the oxidation state of the absorber

Origin of the XANES features



Pre-edge

caused by electronic transitions (mainly dipole allowed) to **empty bound states** near the Fermi level.

Provide information about absorber local geometry and electronic state around the absorber: number of neighbours, ligand symmetry, valence state

Edge (E_o)

defines the onset of **continuous states** (not the Fermi level !)

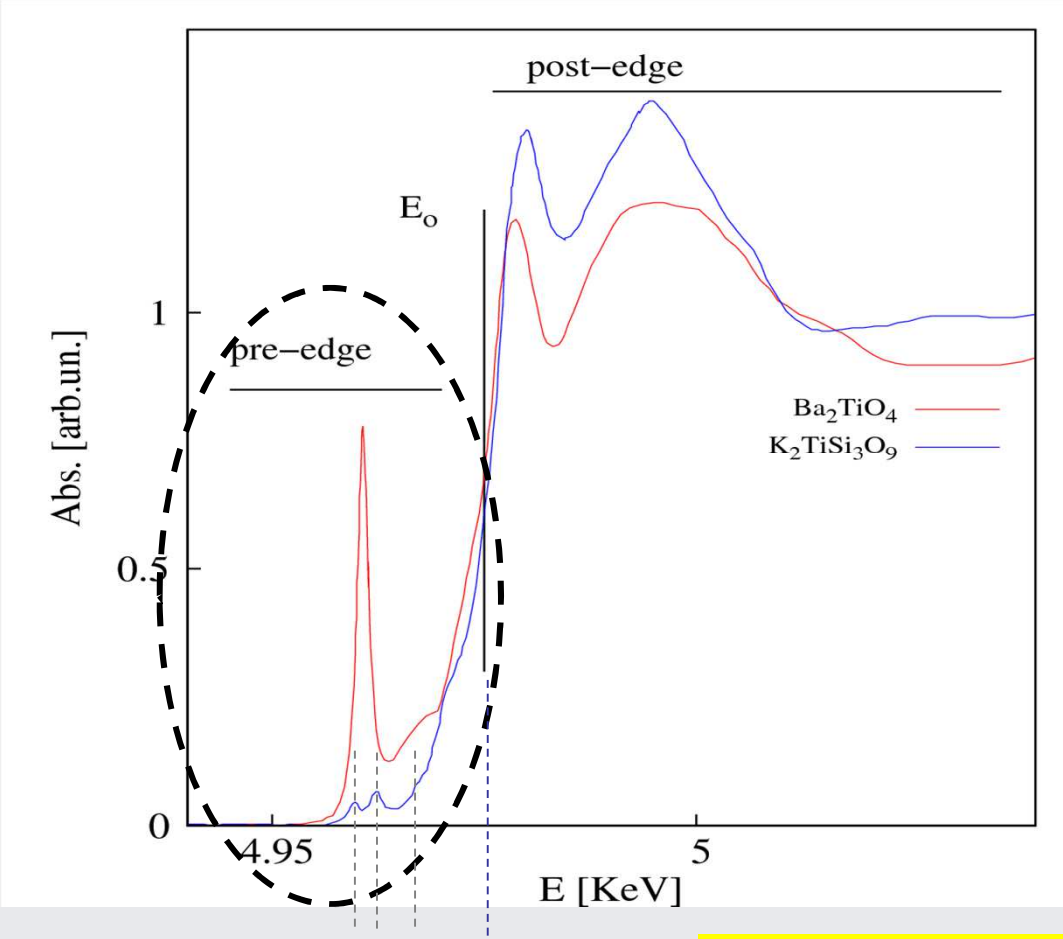
E_o is a function of the absorber oxidation state & binding geometry. It may also increase by several eV per oxidation unit

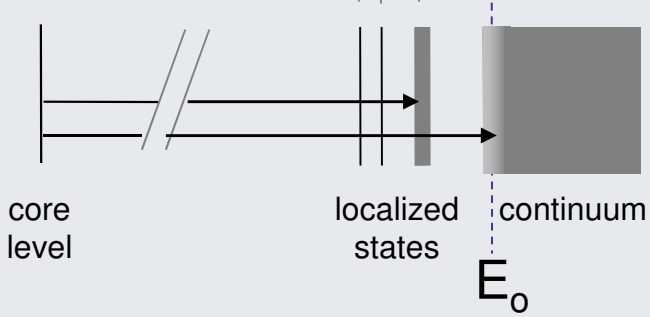
Post-edge (XANES)

multiple scattering features (FMS)

The analysis may provide finest details about local atomic structure and geometry.

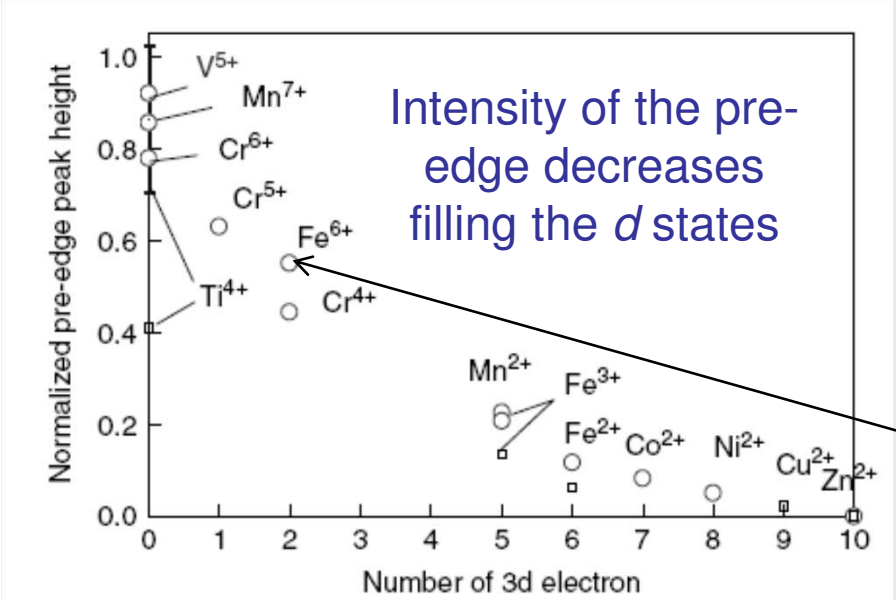
The Pre-edge region





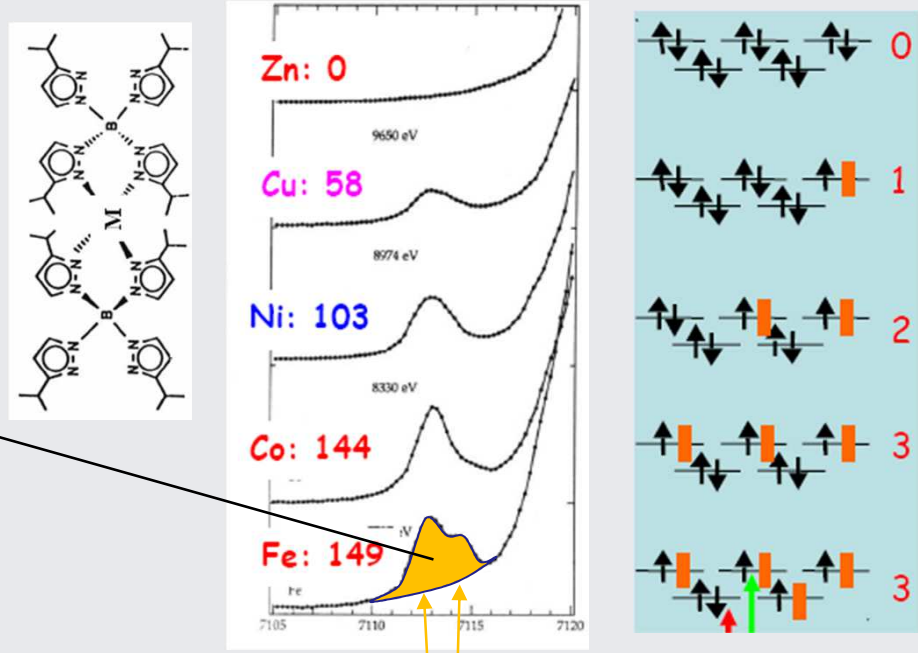
caused by electronic transitions (mainly dipole) to **empty bound states** near the Fermi level.

K edges of 3d metal oxide: intensity vs empty states



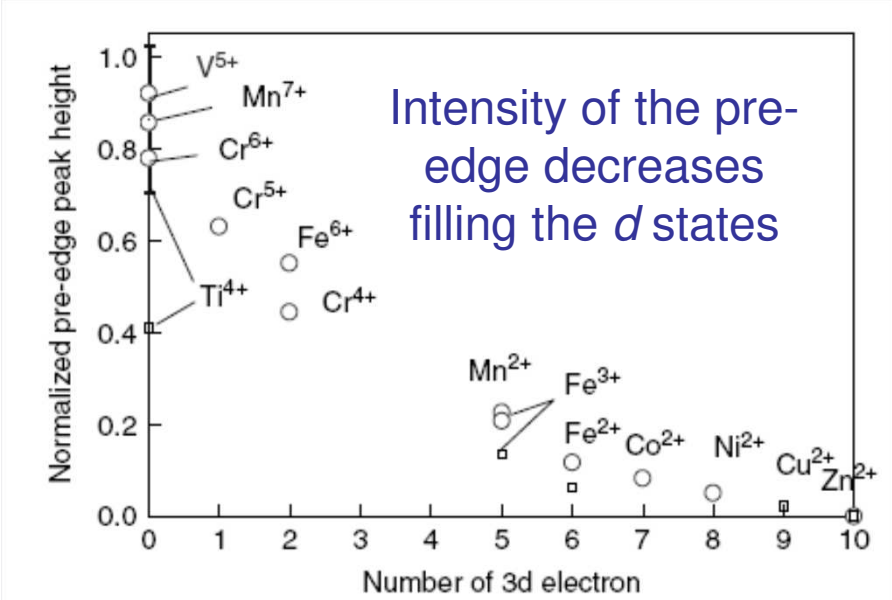
Intensity of the pre-edge decreases filling the *d* states

Example:
Pseudo Tetrahedral Metal Complexes ***M*(B(3-isopropyl-pyrazol-1-yl)4)2**



Pre-edge caused by electronic transitions (mainly dipole) to **<u>empty bound states</u>** near the Fermi level.

K edges of 3d metal oxide: intensity vs empty states



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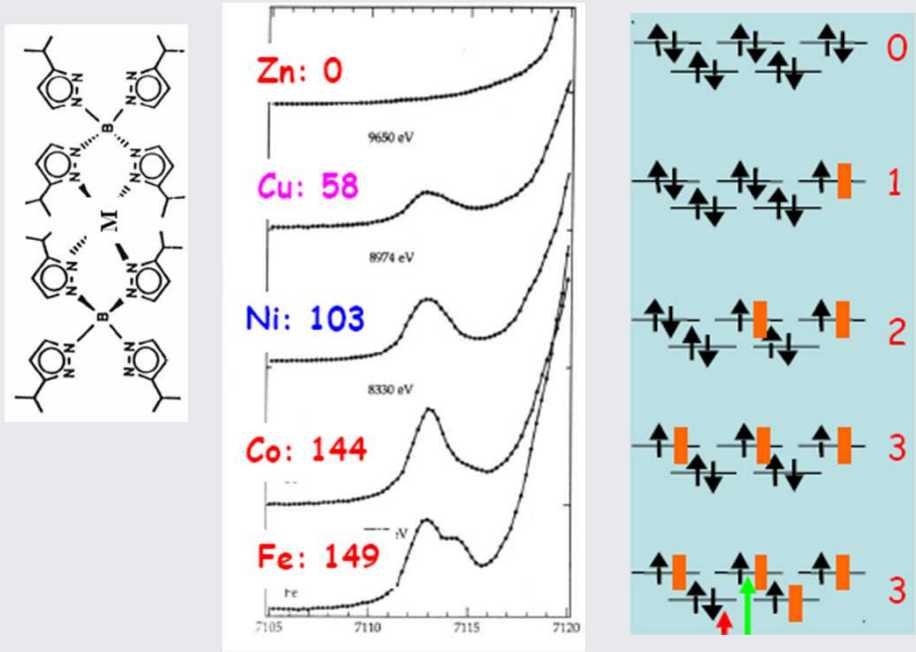
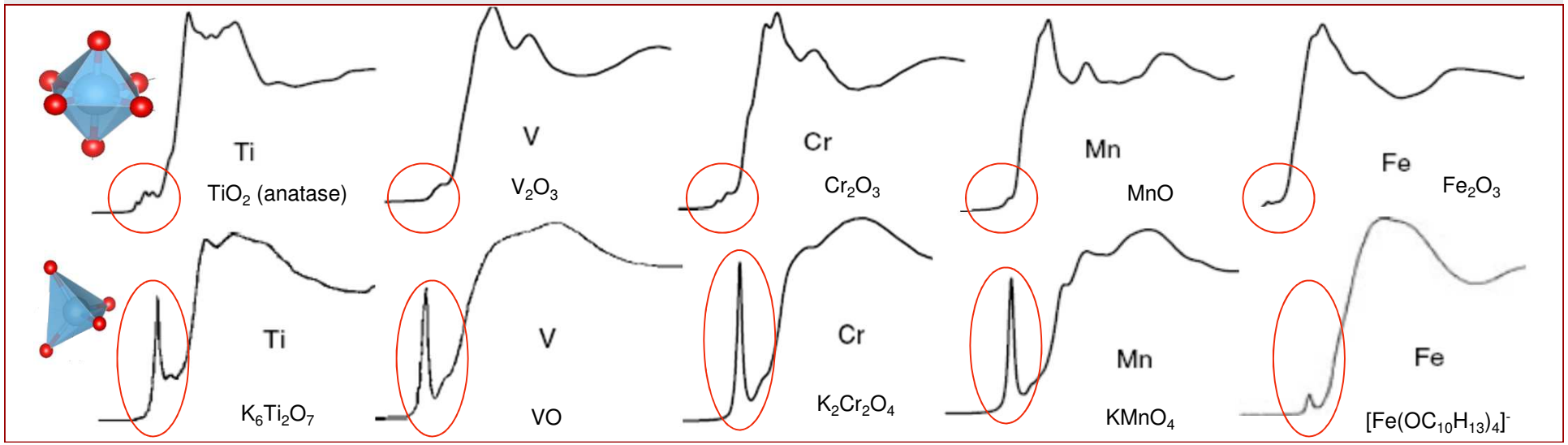
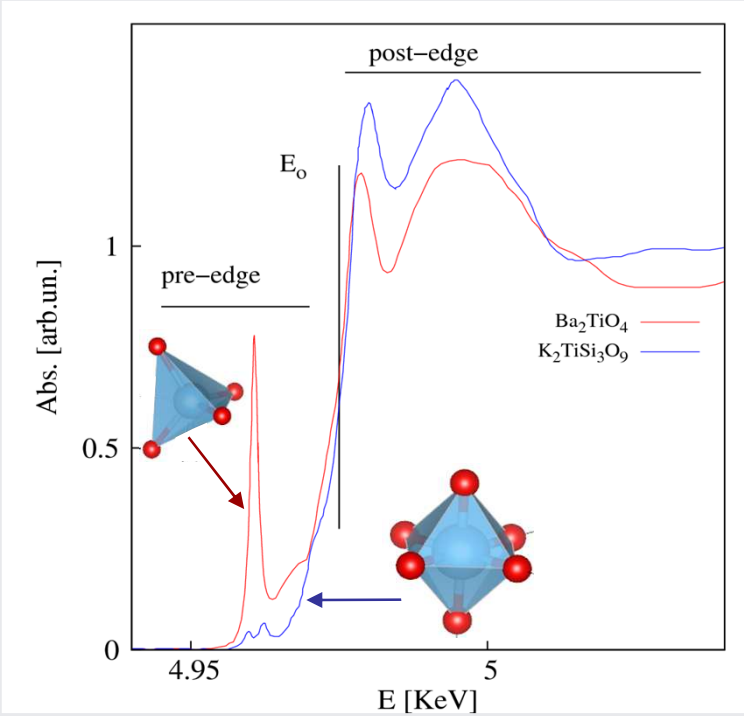
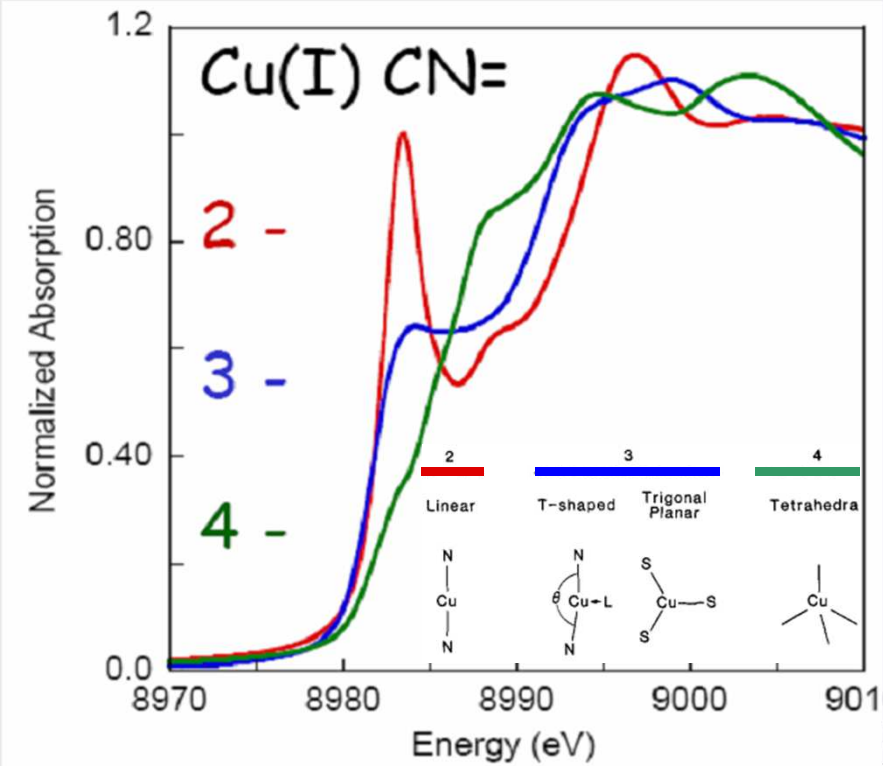




Pre-edge: sharp features signal the transitions to bound electronic levels below the continuum threshold

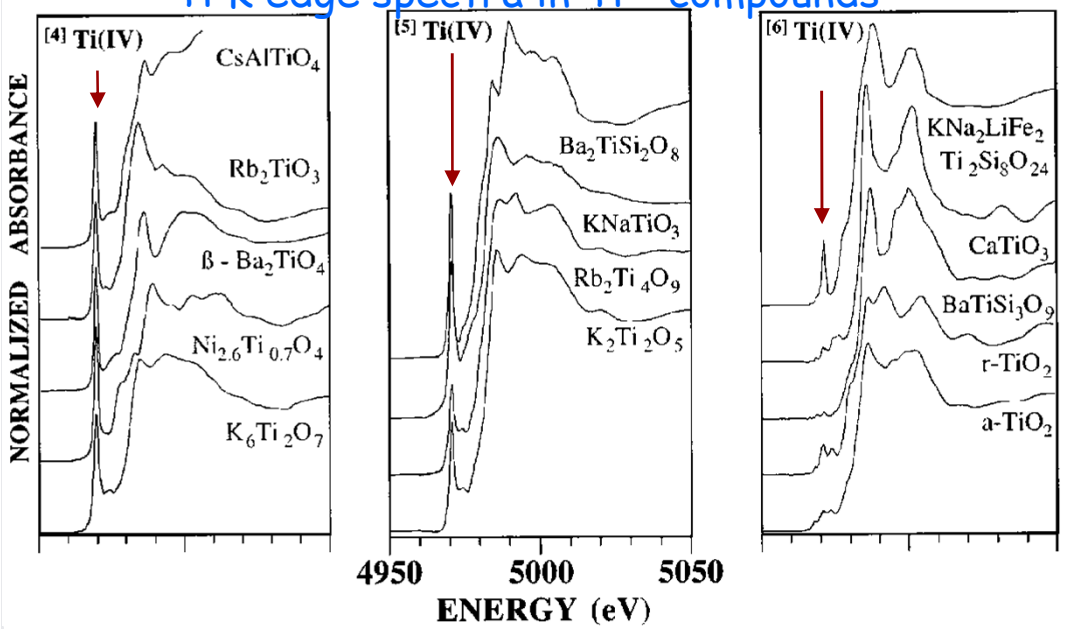


The XANES of the <u>same ions</u>, even in the <u>same oxidation state</u>, may behave <u>definitively different</u> in different compounds!



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

Ti K edge spectra in Ti^{4+} compounds

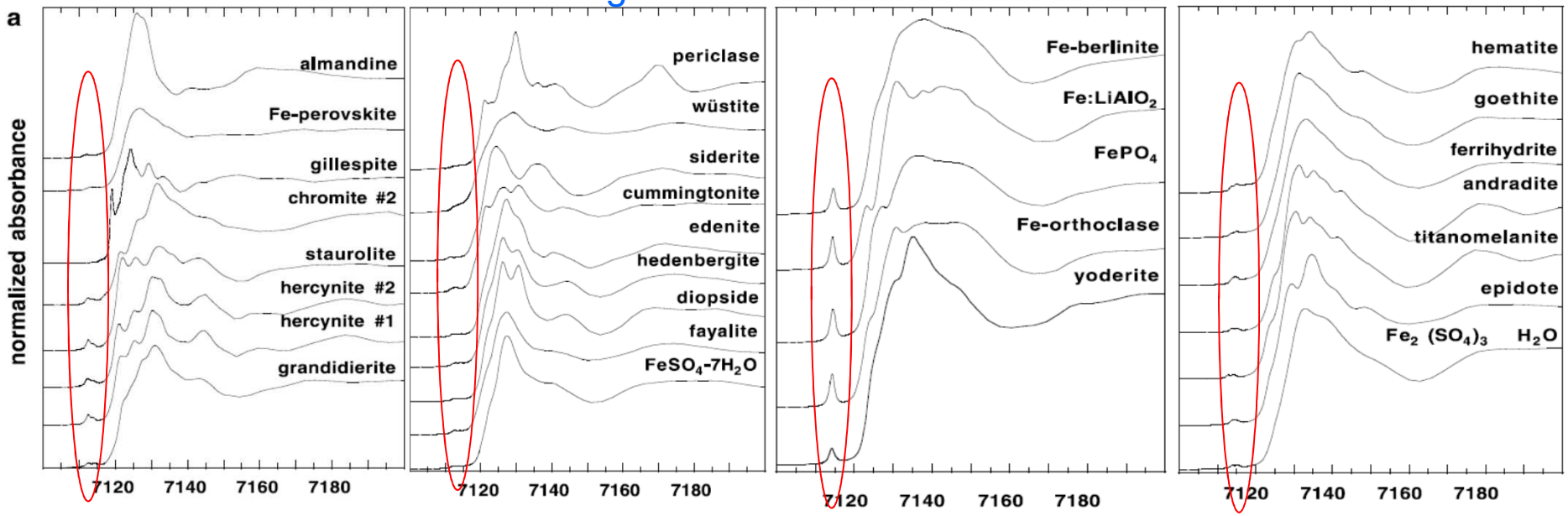


6. Farges F, Brown GE, Rehr JJ. *Geochim. Cosmochim. Acta* 1996; 60: 3023.

Ti K pre-edge peak in **4-**, **5-** and **6-**fold coordinated Ti^{4+} compounds occurs at different energies and have different height/area

Fe K pre-edge looks definitively different as a function of Fe oxidation state and coordination number

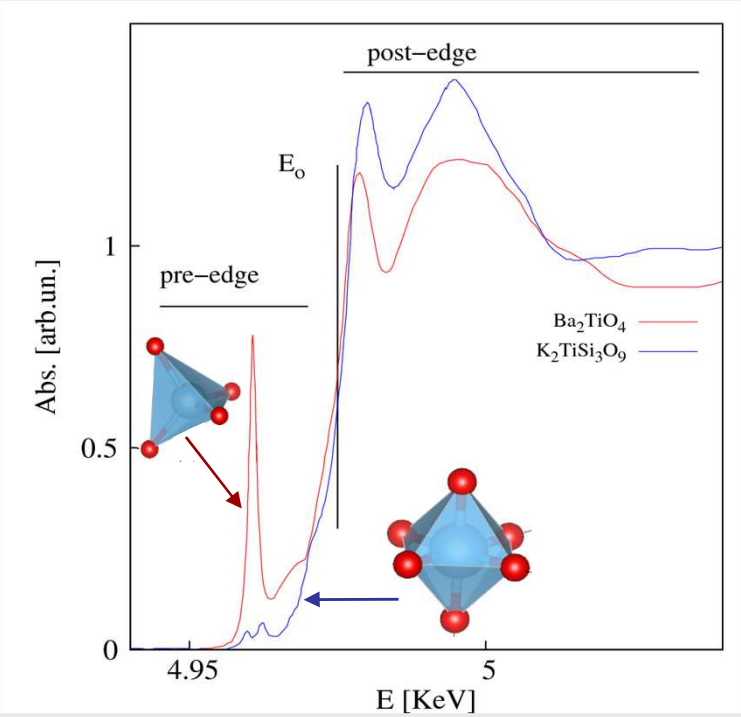
Fe K edges in minerals



Fe^{2+} in 4, 5, 6 coord. sites | Fe^{2+} in 6 coord. sites | Fe^{3+} in 4, 5 coord. sites | Fe^{3+} in 6 coord. sites

M. Wilke, F. Farges et al. *American Mineralogist, Volume 86, pages 714–730, 2001*

Pre-edge: sharp features signal the transitions to bound electronic levels below the continuum threshold



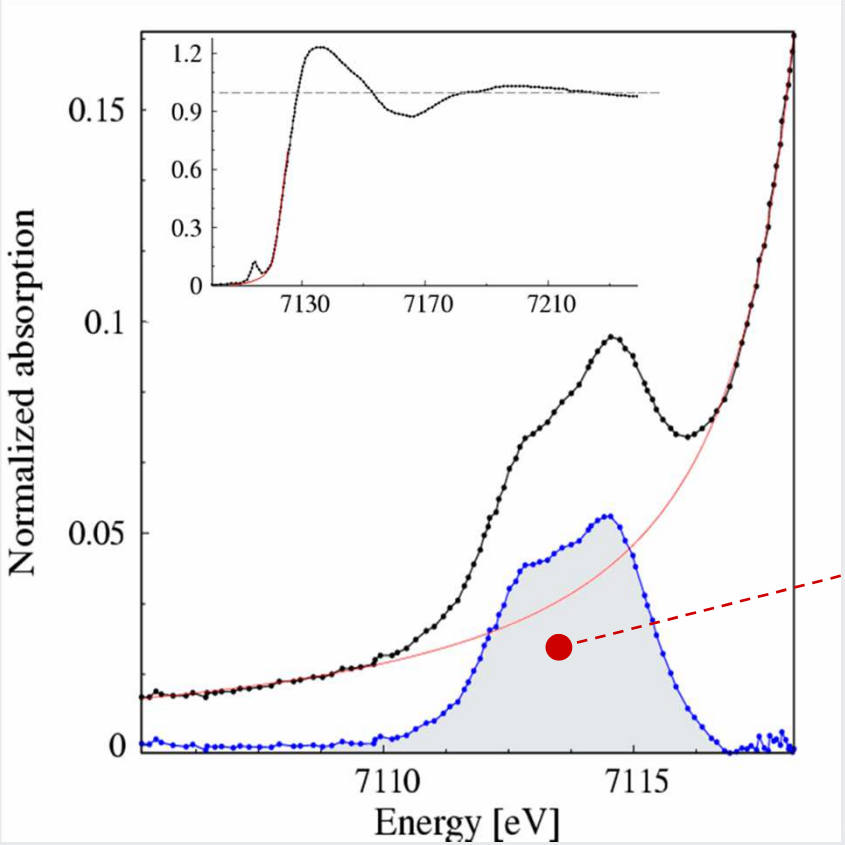
The XANES of the <u>same ions</u>, even in the <u>same oxidation state</u>, may behave <u>definitively different</u> in different compounds!

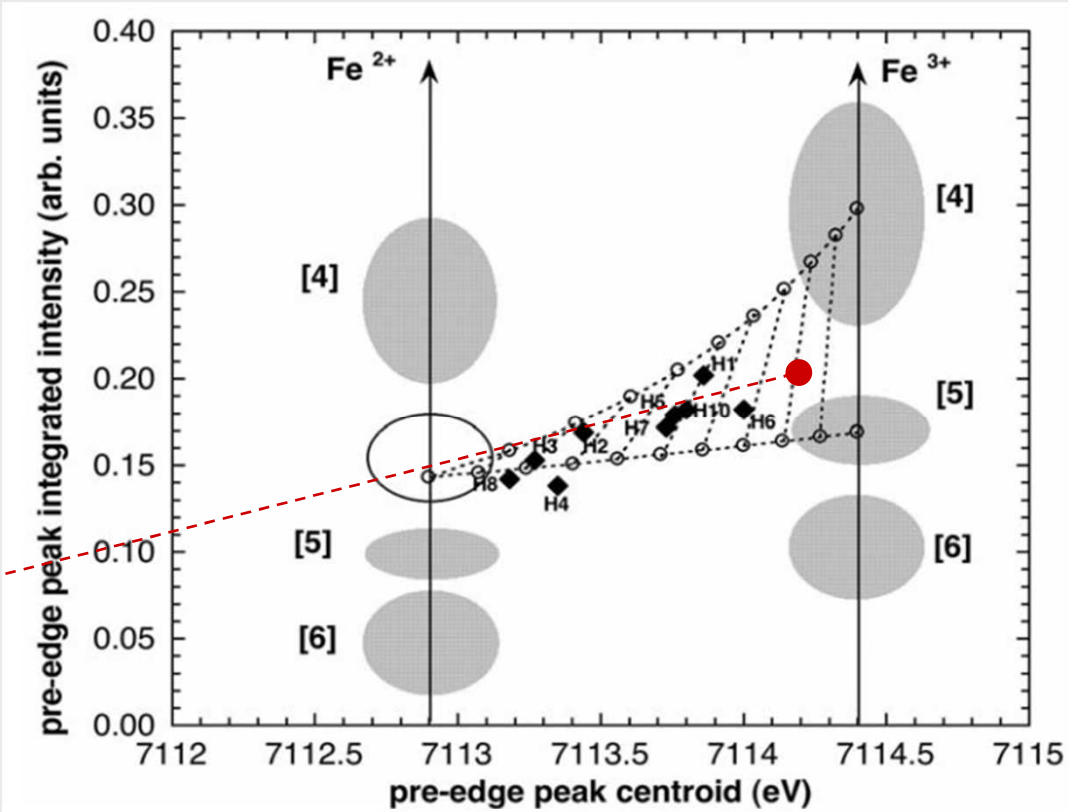
<u>Quantitative Models</u>: multiplet theory

<u>Semi-quantitative approaches</u>:

- Comparison with model compounds
- Molecular orbital symmetry (group theory)

The case of Fe: average valence and coordination from the pre-edge peak shape





G. Giuli et Al. *Meteoritics & Planetary Science* 40, Nr 11, 1575–1580 (2005)

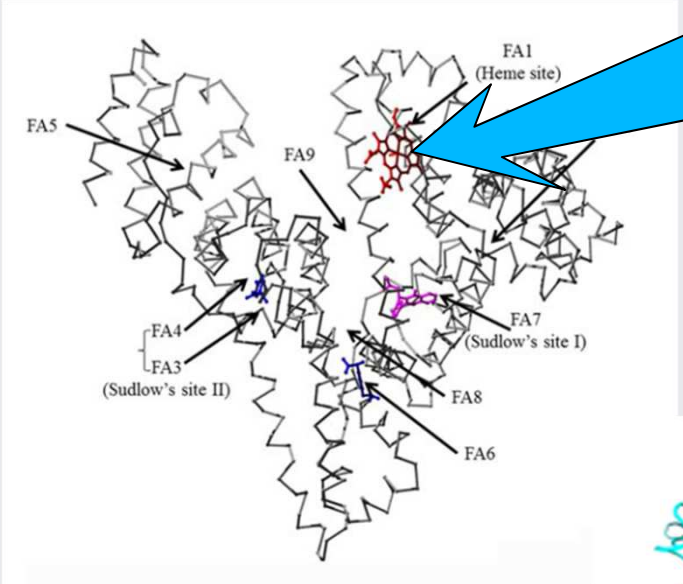
Pre-edge peak area *vs* position is related to valence state and coordination number of Fe absorbers

From Fe K pre-edge centroid position and peak area it is possible to individuate the average Fe valence state and coordination number

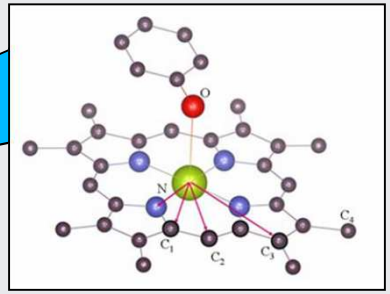
Fe values from Fe reference compounds: M. Wilke, F. Farges et al. *American Mineralogist, Volume 86, pages 714–730, 2001*

The case of Fe:

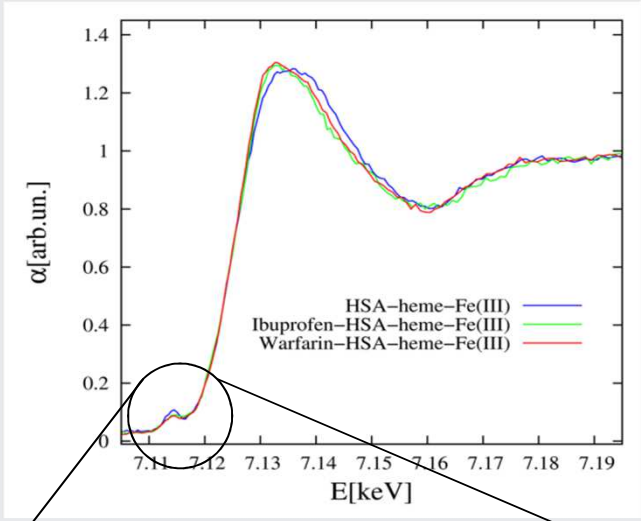
Ibuprofen/warfarin induce V to VI Fe coordination transition in HSA

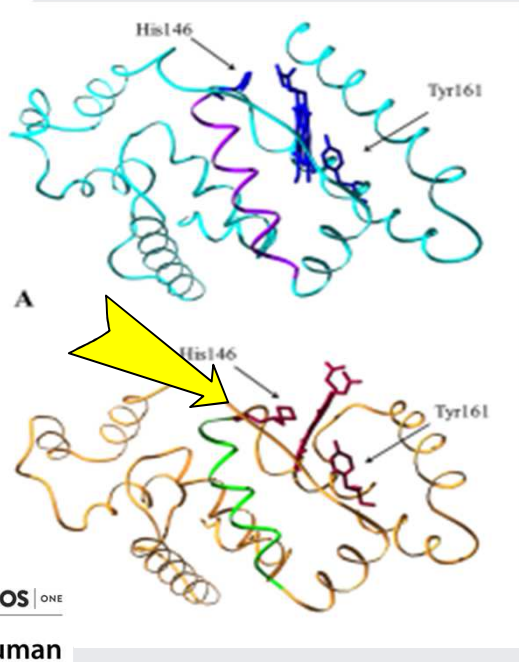


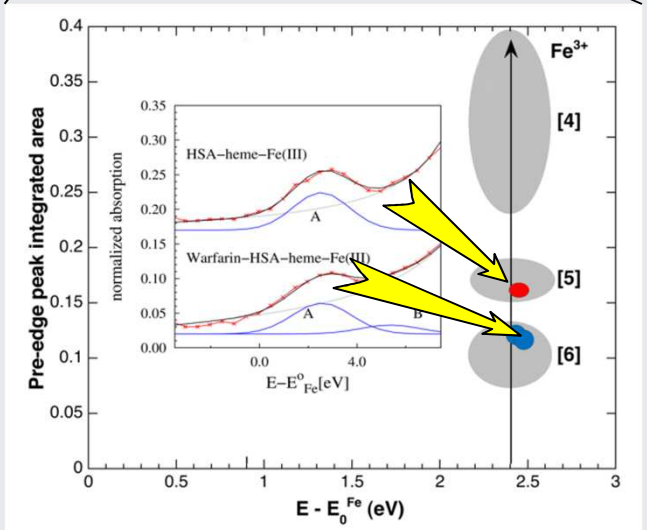
Human Serum Albumin



Heme (Fe) site







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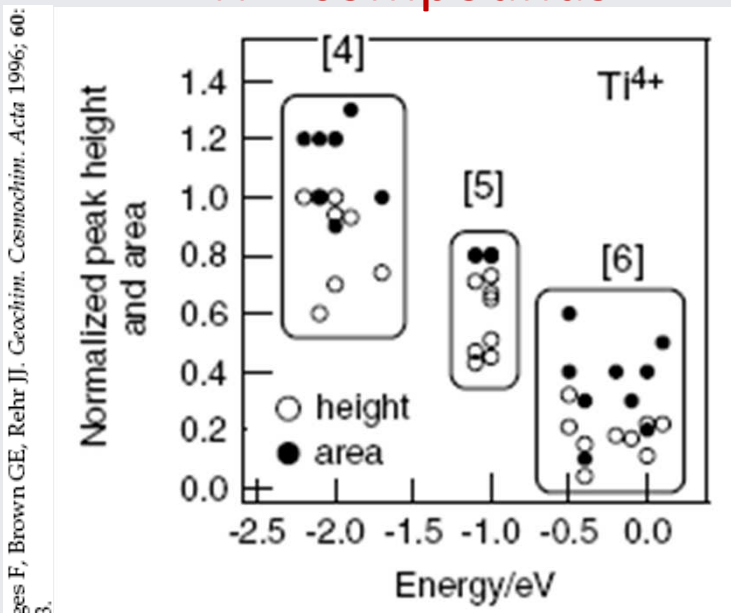
The Five-To-Six-Coordination Transition of Ferric Human Serum Heme-Albumin Is Allosterically-Modulated by Ibuprofen and Warfarin: A Combined XAS and MD Study

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]

...and Ti, V, ...: average valence and coordination from the pre-edge peak shape

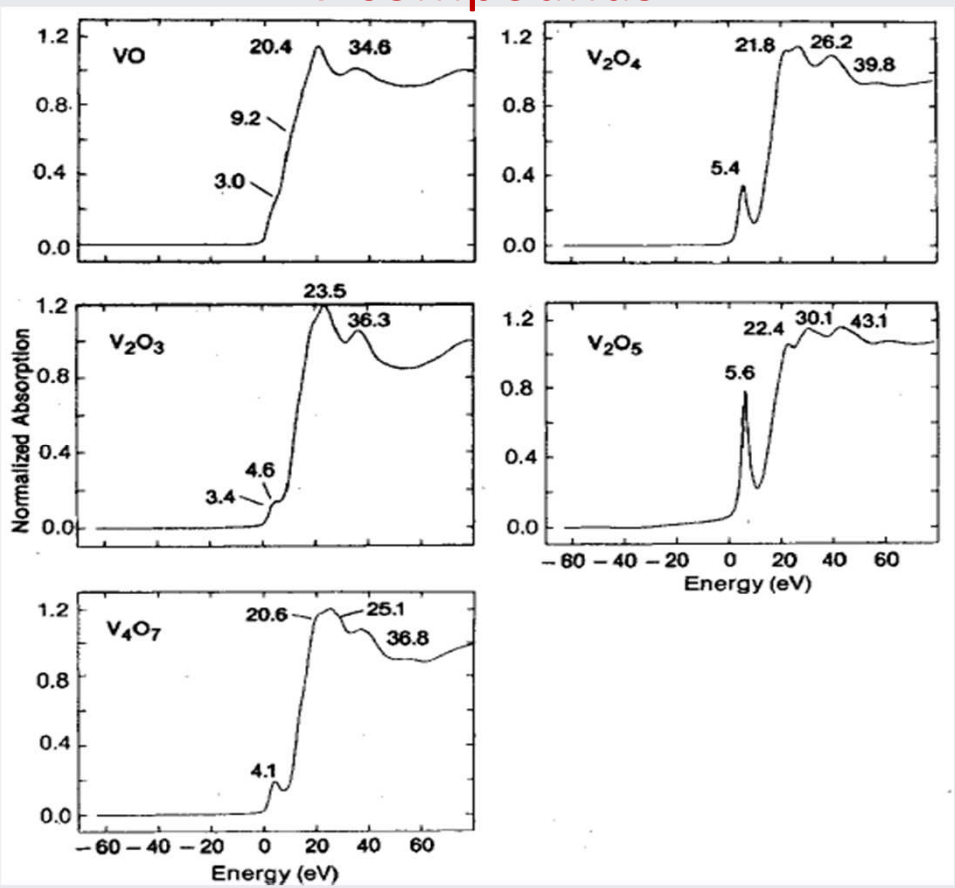
Ti^{4+} compounds



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

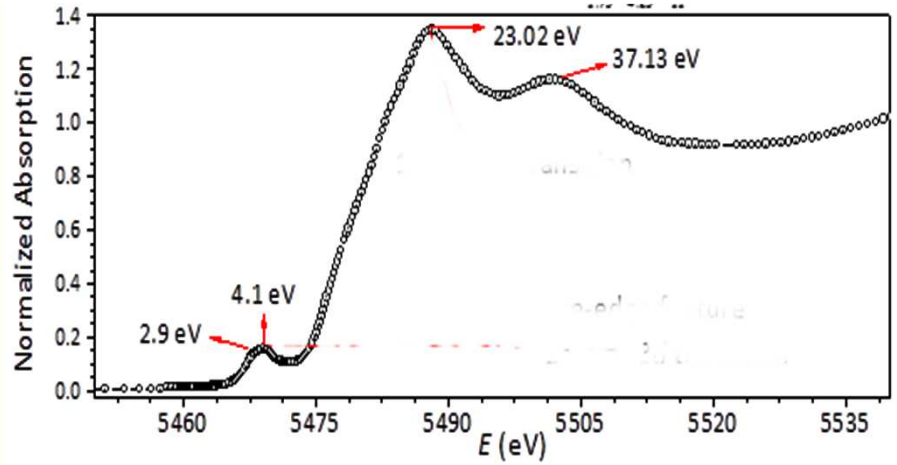
Ti pre-edge main peak intensity and area as a function of coordination number

V compounds

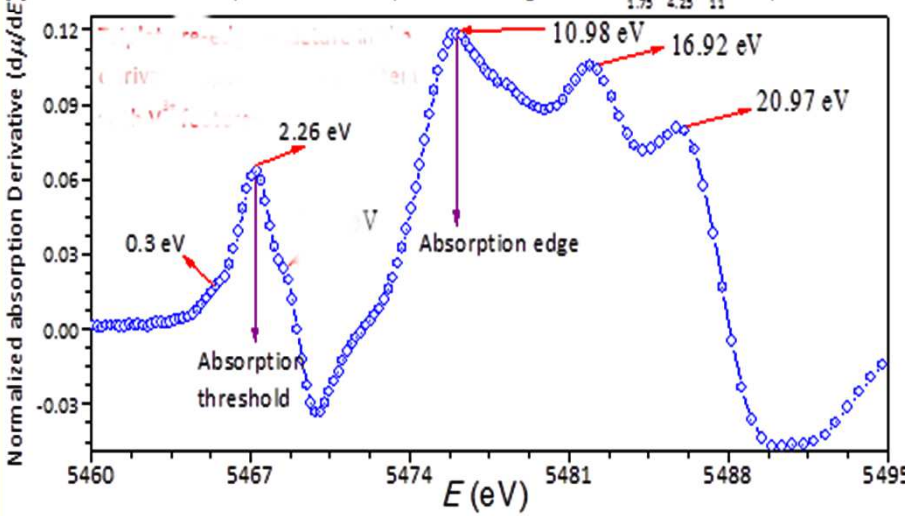


It is possible to understand the absorber coordination looking at the intensity/area of pre-edge peaks in comparison with reference compounds data

$PbFe_{1.75}V_{4.25}O_{11}$

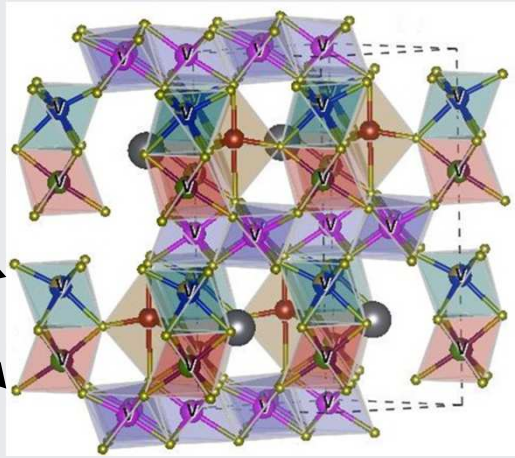


Absorption derivative plot of V *K*-edge of $PbFe_{1.75}V_{4.25}O_{11}$ sample

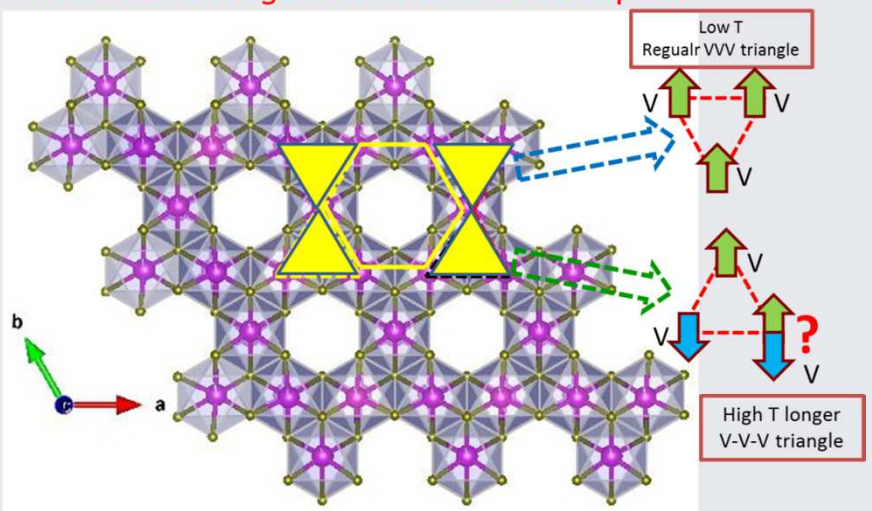


V-valence state

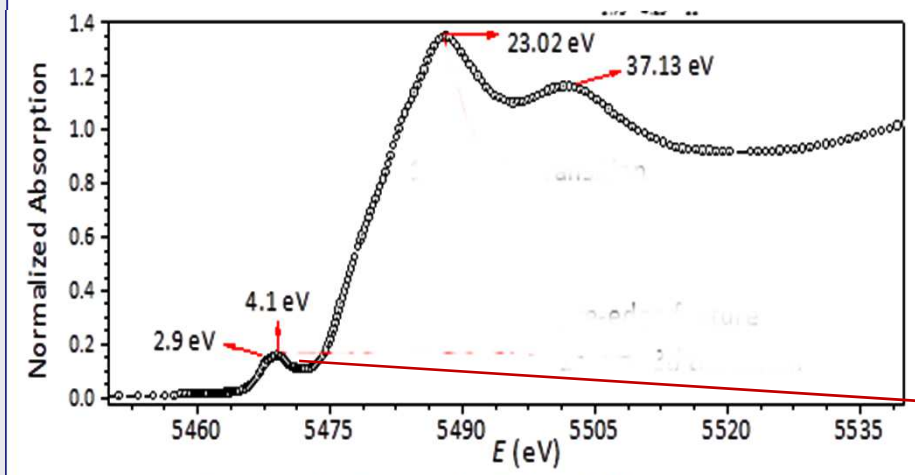
$FeVO_9$ dimer having mixed Fe^{3+}/V^{4+} occupancy



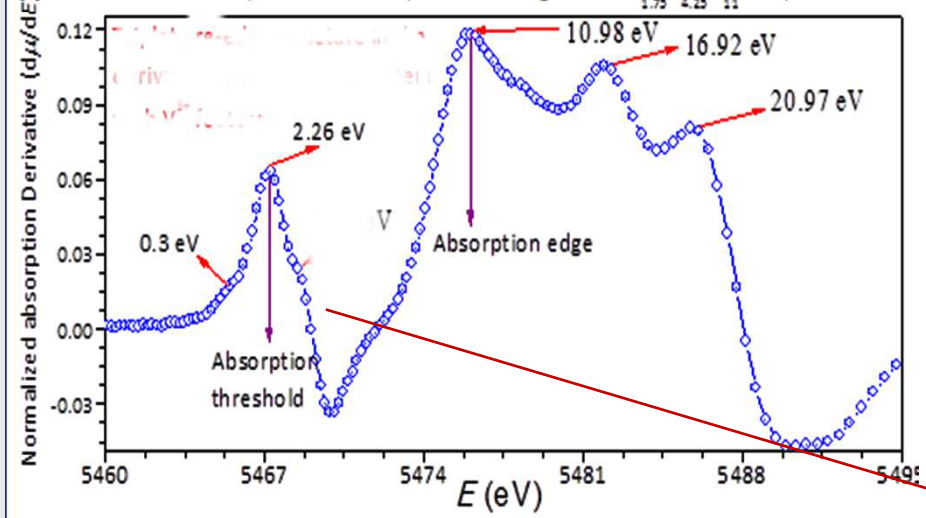
Formation of *kagome trimer* in the *a-b* plane

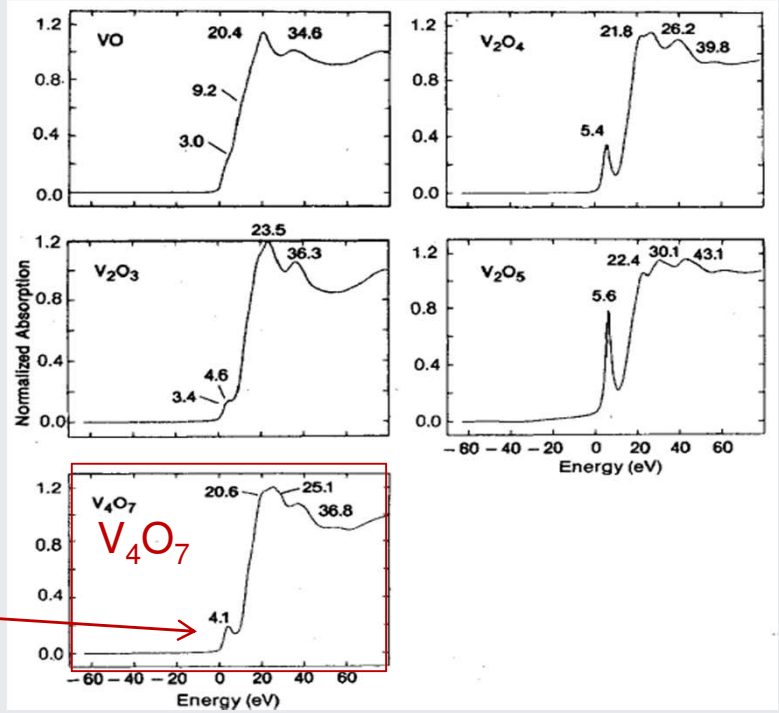


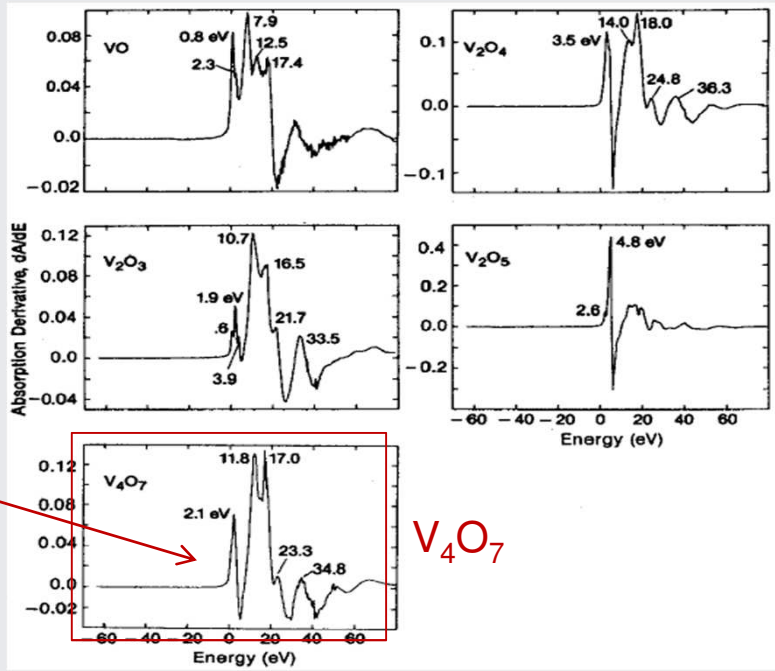
$PbFe_{1.75}V_{4.25}O_{11}$



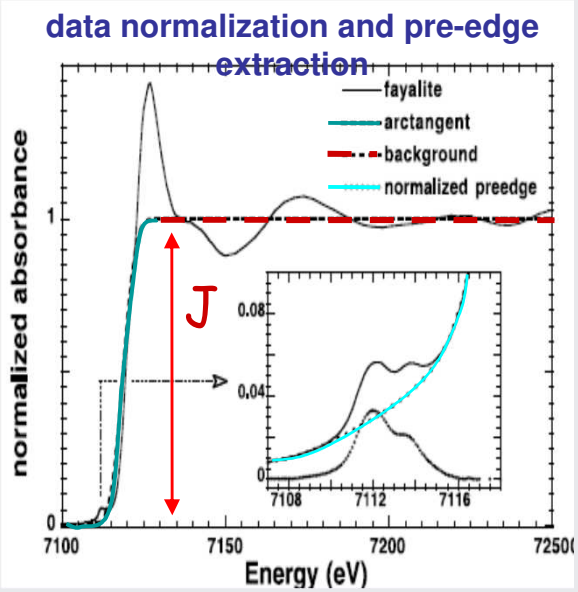
Absorption derivative plot of V K-edge of $PbFe_{1.75}V_{4.25}O_{11}$ sample

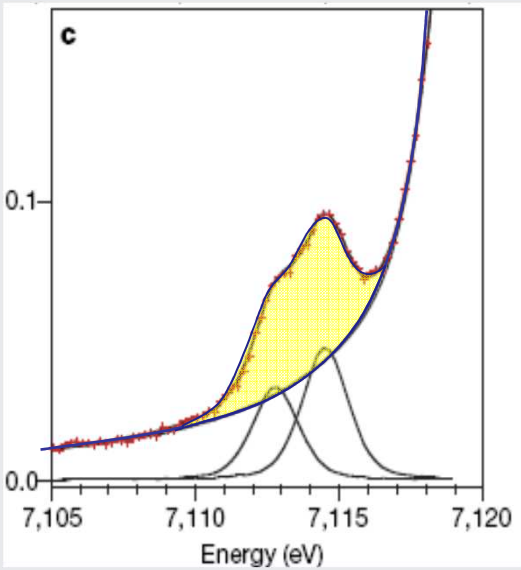


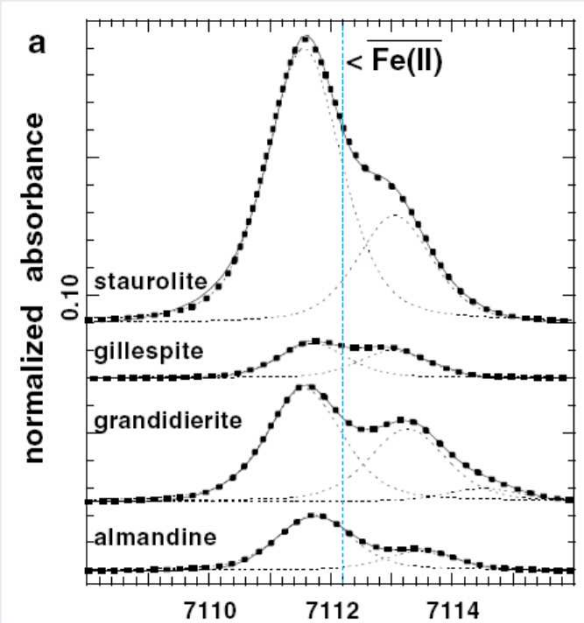


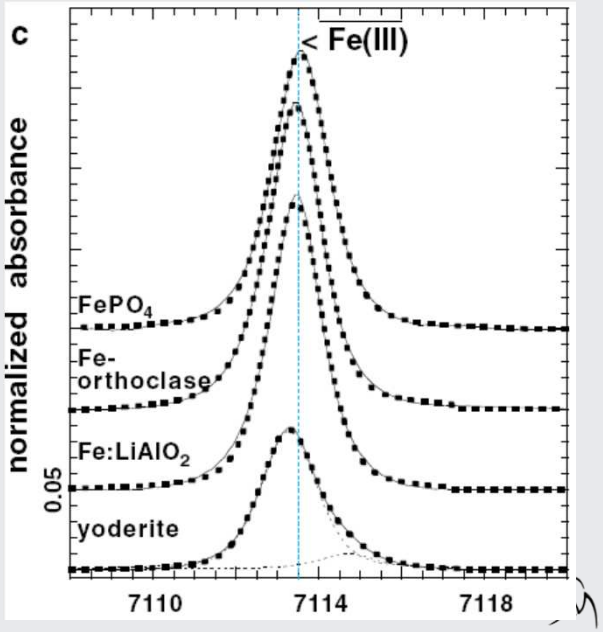


Deconvolution of pre-edge features









normalization: Jump = 1

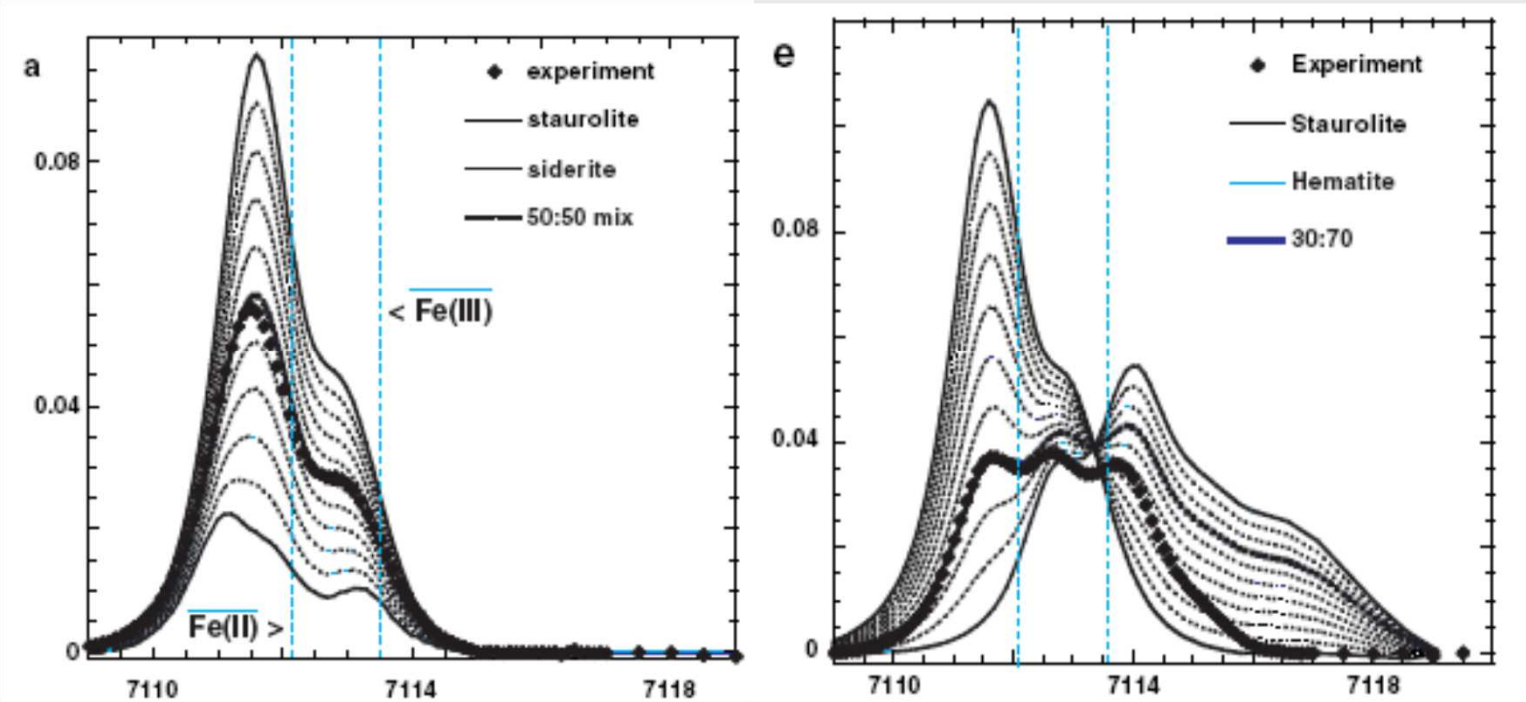
arctangent: transitions to continuum states,

peaks: transitions to localized states:

Pseudo-Voigt shaped peaks take into account for the convolution of true peak shape (Lorentzian contribution) with the experimental energy resolution (Gaussian contribution)

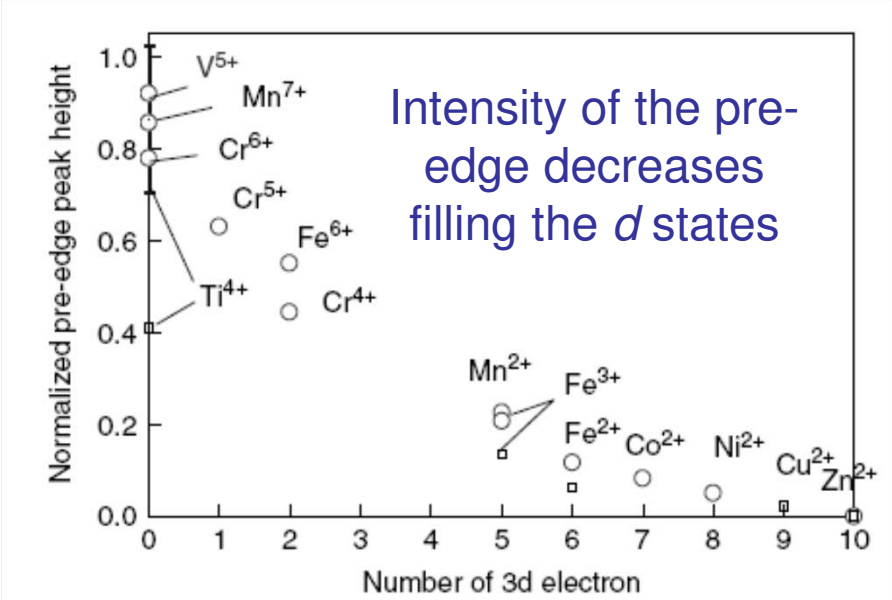
M. Wilke, F. Farges et al. *American Mineralogist, Volume 86, pages 714–730, 2001*

linear combination of reference XANES spectra (LCA)



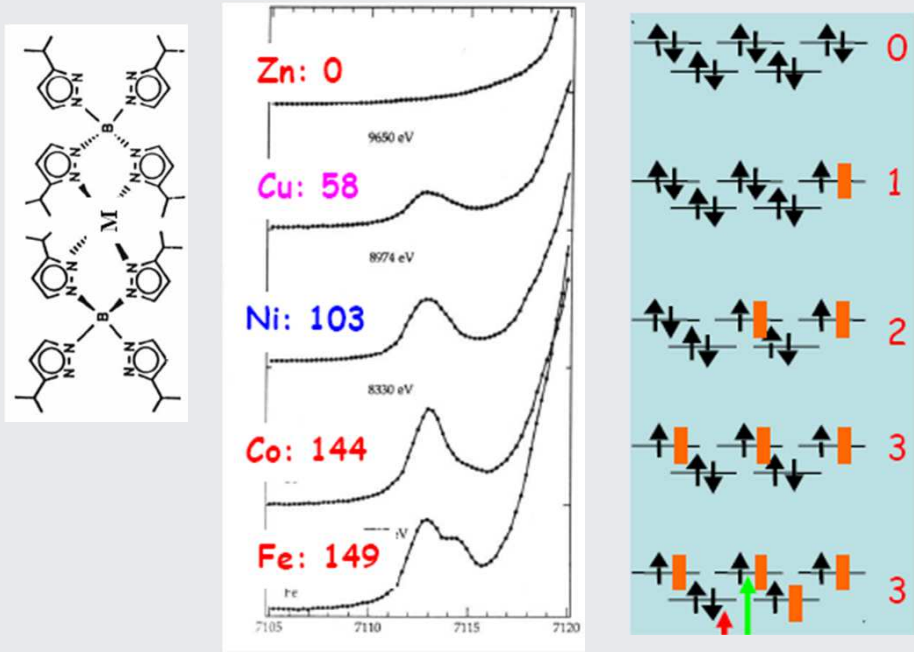
Model compounds data can be used to understand the oxidation states and local coordination environments of the absorber in composite or multiphase materials

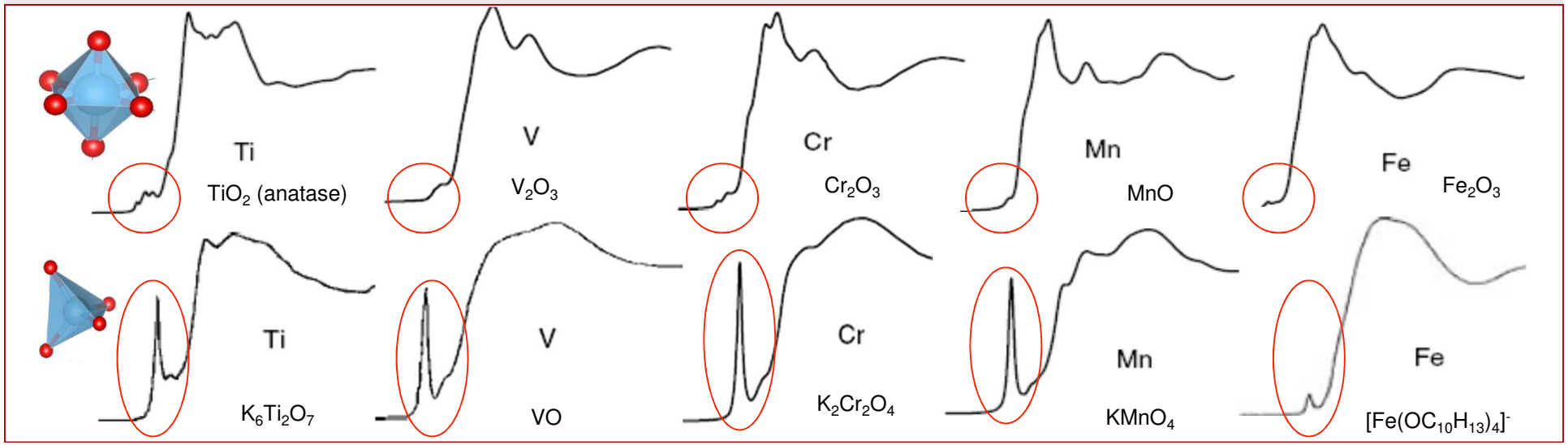
K edges of 3d metal oxides.... S-d Q-transition?



Example:

Pseudo Tetrahedral Metal Complexes ***M*(B(3-isopropyl-pyrazol-1-yl)4)2**

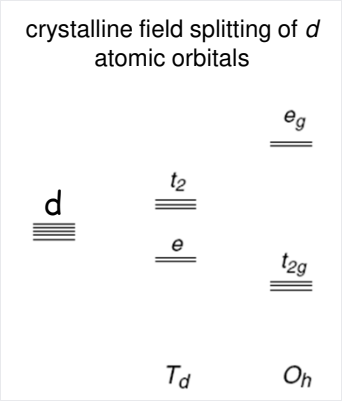




K edge: mainly s → p transitions

I_{sd} (quadrupole) ~ 10^{-2} I_{sp} (dipole)

Hybridization mixes *p-d* states then dipole allowed transitions occur to empty p-components of hybrid *pd* levels



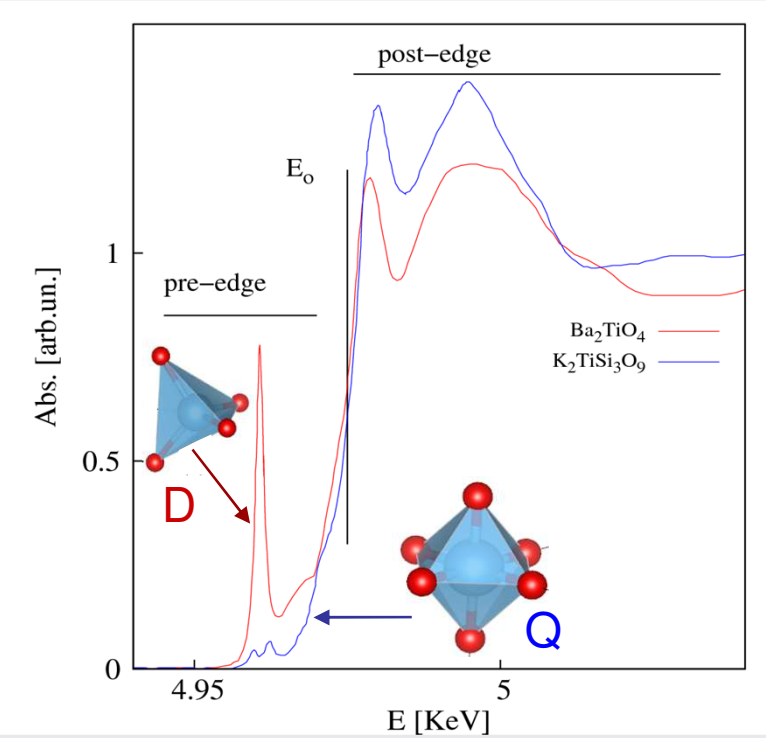


Table 1. Lists of irreducible representations and the relating functions in T_d, O_h, and D_{4h} point groups

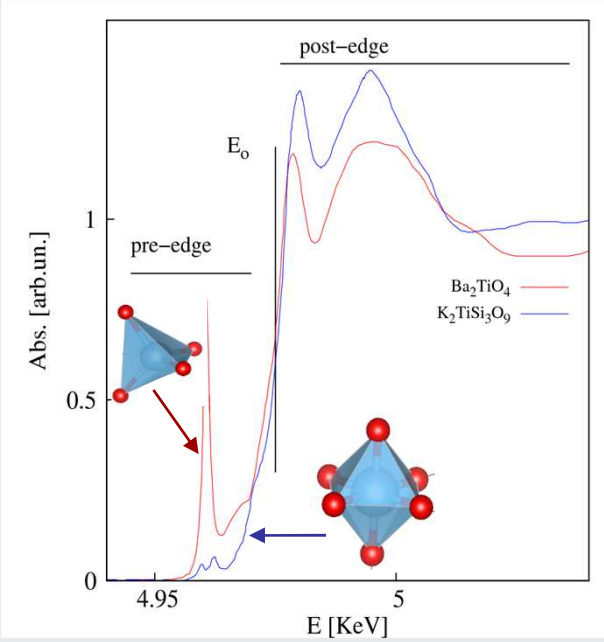
T_d	p	d
A_1		$x^2+y^2+z^2$
A_2		
E		$(2z^2-x^2-y^2, x^2-y^2)$
T_1	(R_x, R_y, R_z)	
T_2	(x, y, z)	(xz, yz, xy)

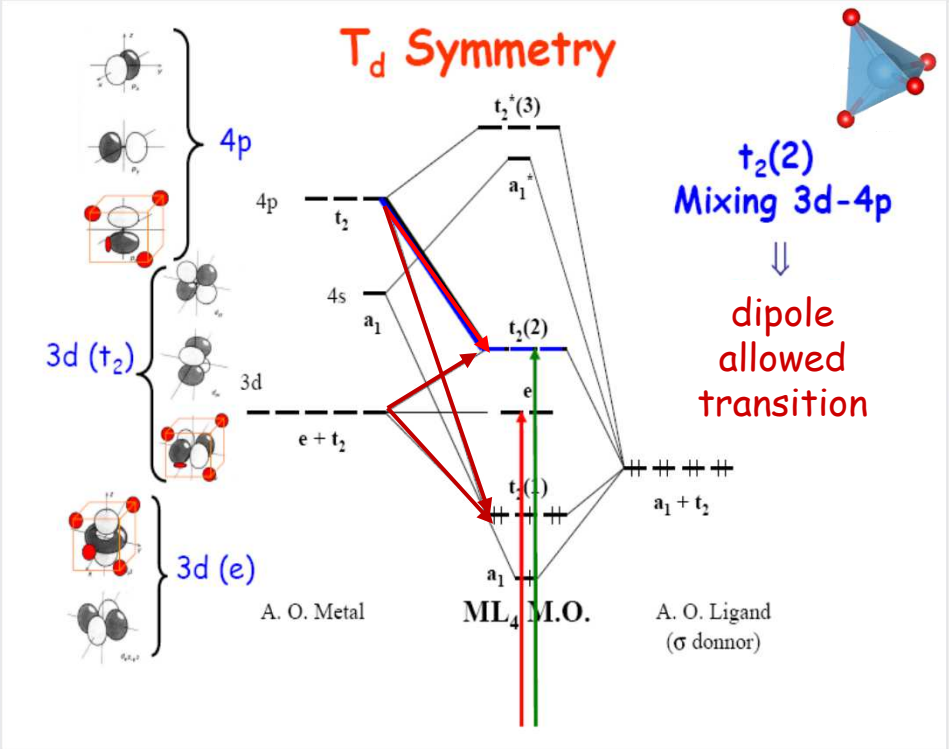
O_h	p	d
A_{1g}		$x^2+y^2+z^2$
A_{2g}		
E_g		$(2z^2-x^2-y^2, x^2-y^2)$
T_{1g}	(R_x, R_y, R_z)	
T_{2g}		(xz, yz, xy)
A_{1u}		
A_{2u}		
E_u		
T_{1u}	(x, y, z)	
T_{2u}		

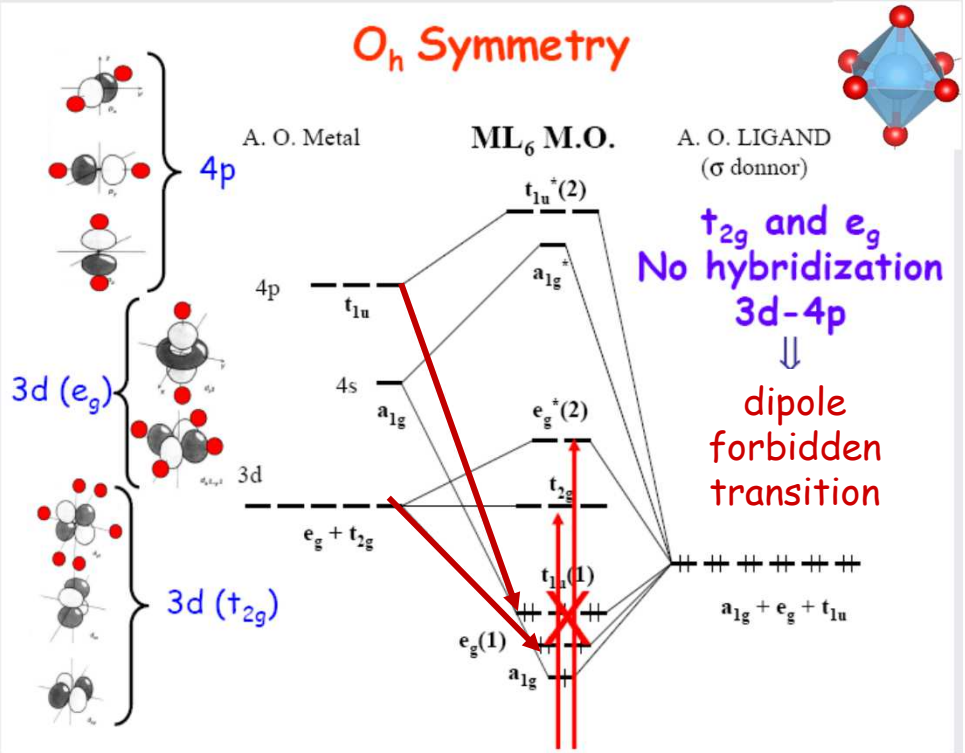
Yamamoto *X-Ray Spectrom.* 2008; **37**: 572–584

Geometrical origin of pre-edge peaks in Ti oxides

Hybridization mixes *p-d* states then dipole allowed transitions occur to **empty** p-components of hybrid *pd* levels

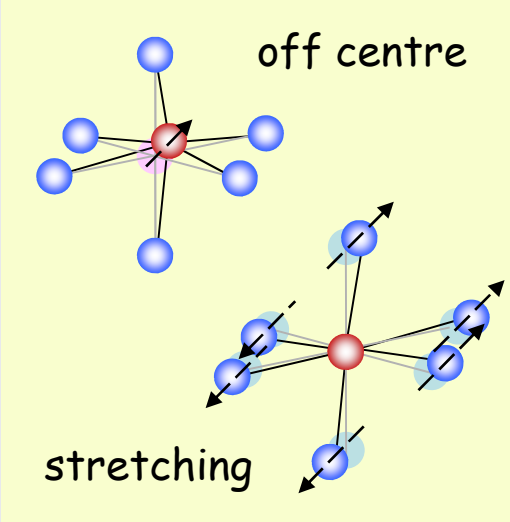




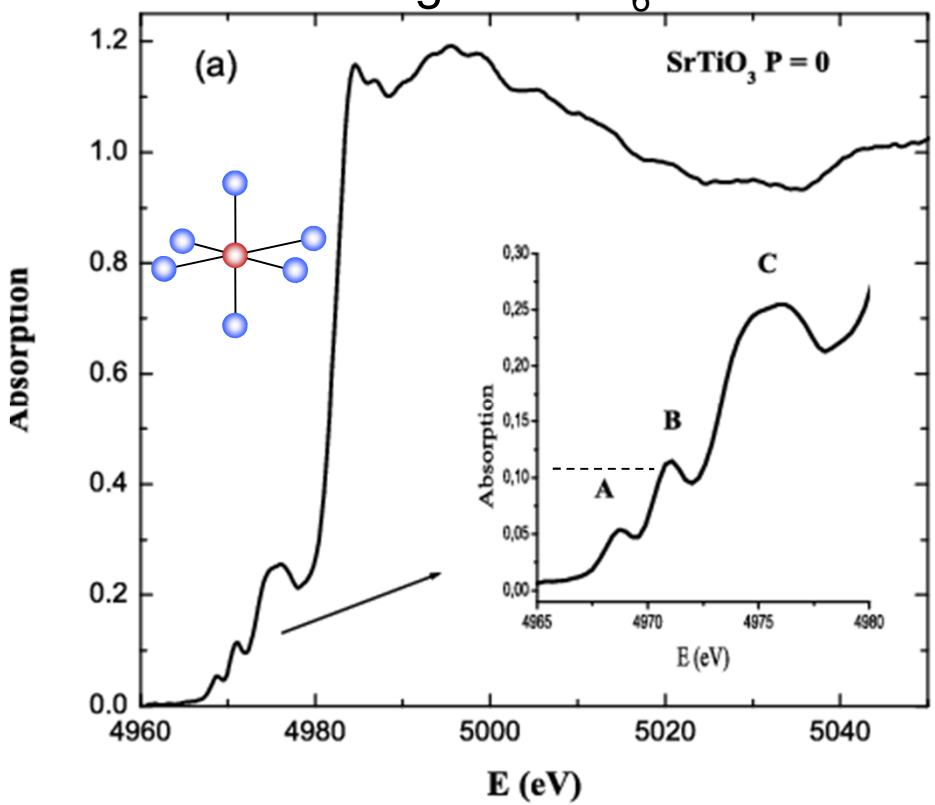


p-d mixing and sensitivity to local symmetry of TiO_6 units

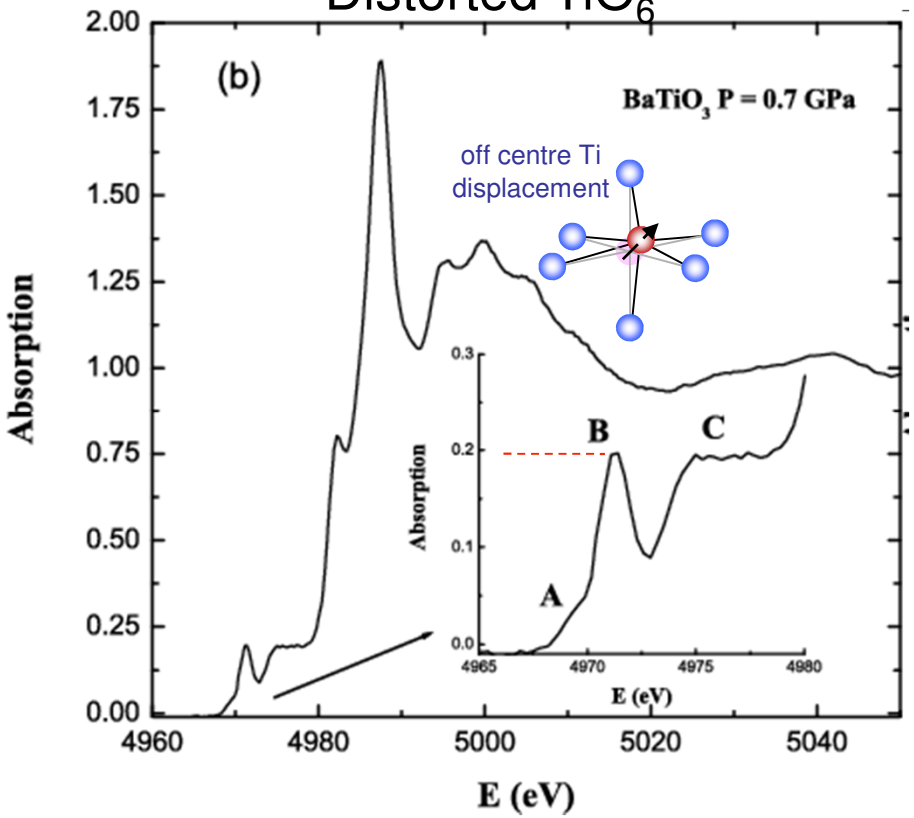
Off centre displacement and stretching of the octahedron decreases the local symmetry (non-centro-symmetric) allowing some degree of *p-d* mixing, this affect the pre-edge peaks intensity

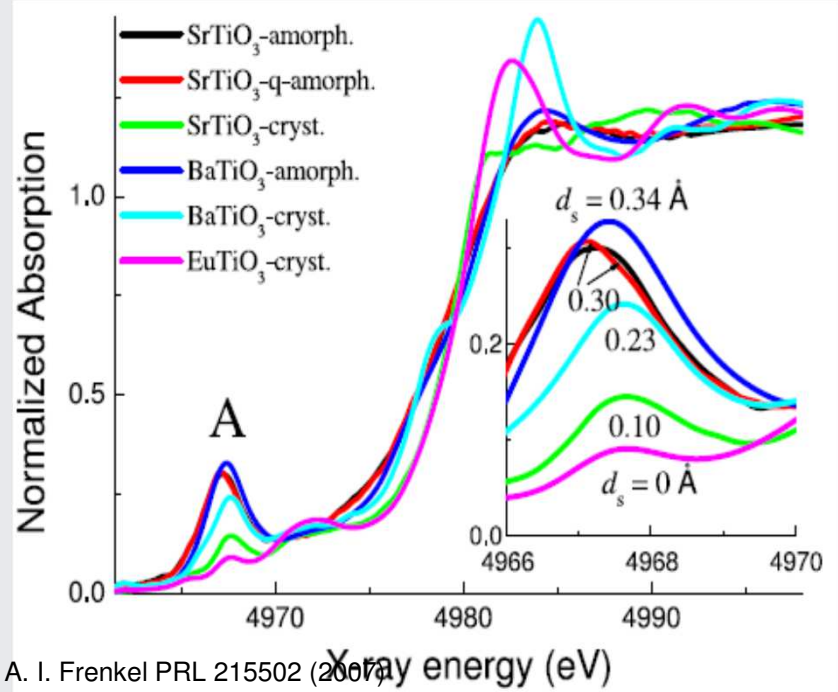


Regular TiO_6



Distorted TiO_6





A. I. Frenkel PRL 215502 (2007)

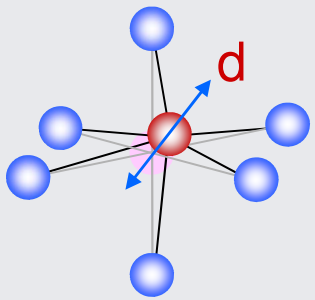
In perovskite structures [1] the area of peak A is proportional to the square of the off center displacement:

$$A = \gamma\, d^2 / 3$$

for Ti $\gamma = 11.2\text{-}13.6$ eV/Å

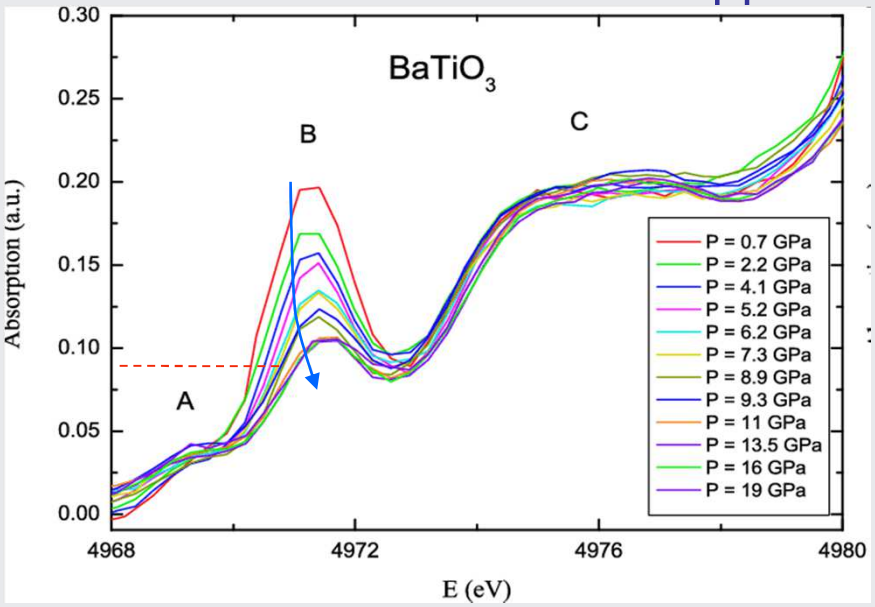
the displacement d contains a static plus a dynamic contribution:

$$d^2 = d_s^2 + d_t^2$$



[1] R.V. Vedrinskii et al. J. Phys. Condens. Matter **10**, 9561 (1998).

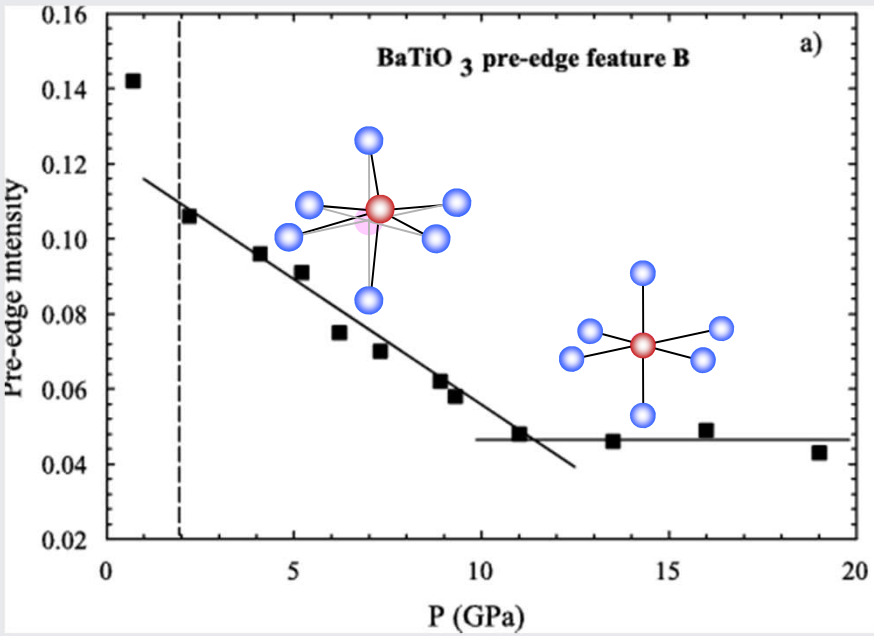
Example: hydrostatic pressure reduces TiO_6 distortions in $BaTiO_3$ and suppress ferroelectricity



The decrease of B peak intensity signals the reduction of Ti atom displacement.

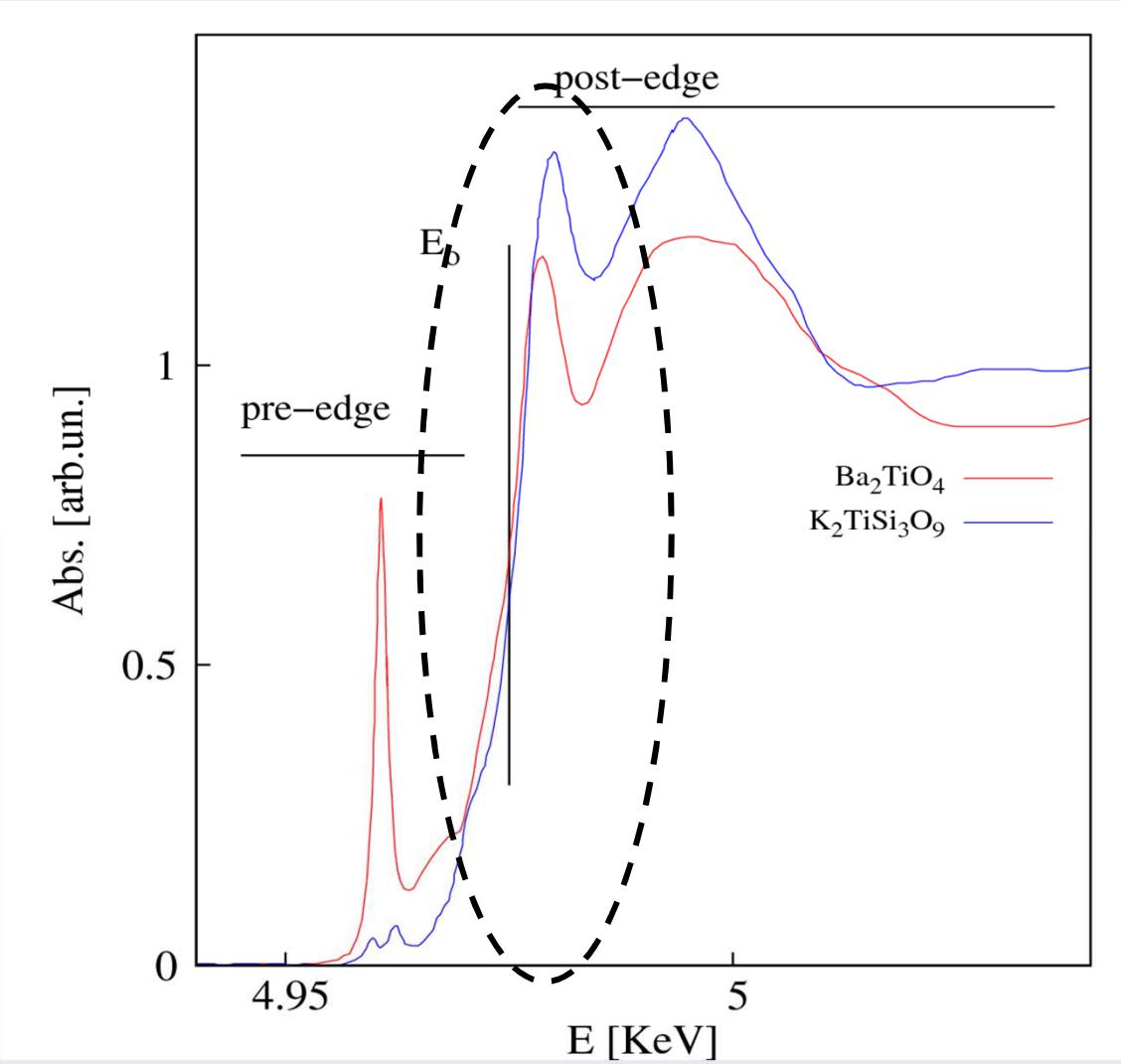
Above 10 GPa Ti must be at the center of a regular oxygen octahedron,

the hybridization of the Ti 3*d* electronic states with the 2*p* electronic states of the surrounding oxygen is at the minimum

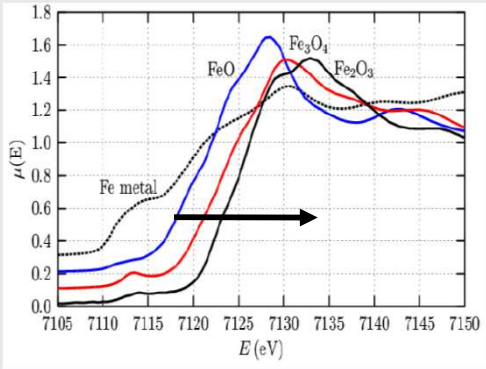


Europhys. Lett., **74** (4), pp. 706–711 (2006)
DOI: 10.1209/epl/i2006-10020-2 J. P. Itié et al.

The Edge region

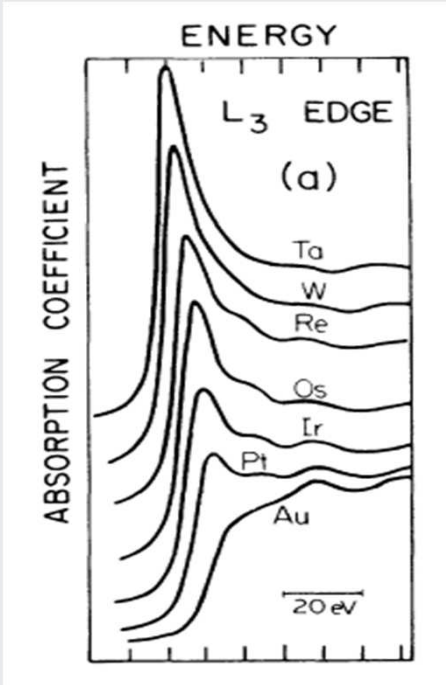


The edge position



oxidation state

The white lines

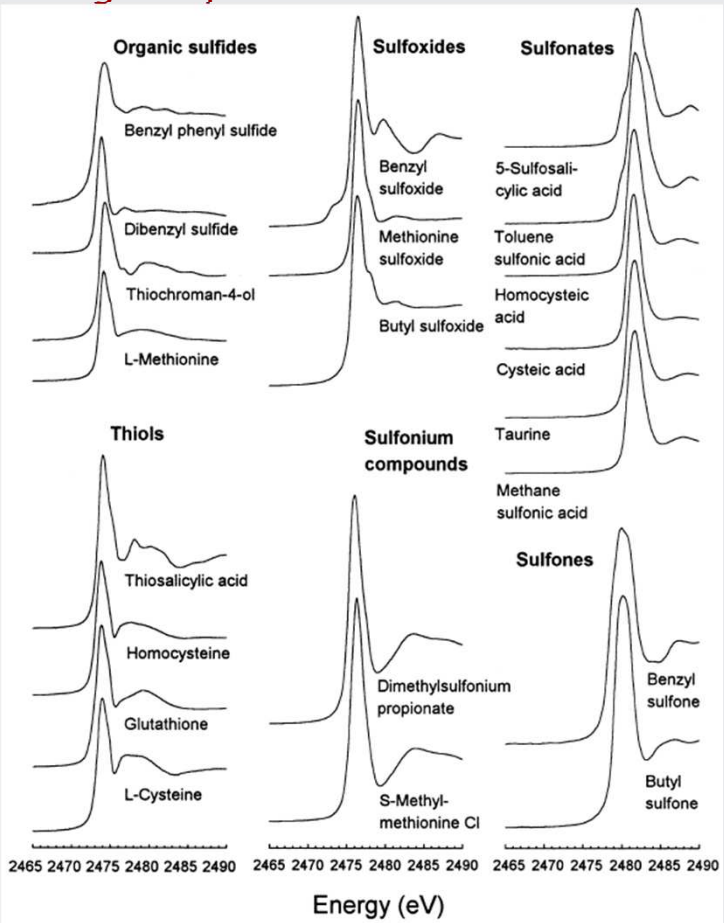


DoS

Edge region: a valuable fingerprint for chemical speciation (coordination geometry and oxidation state)

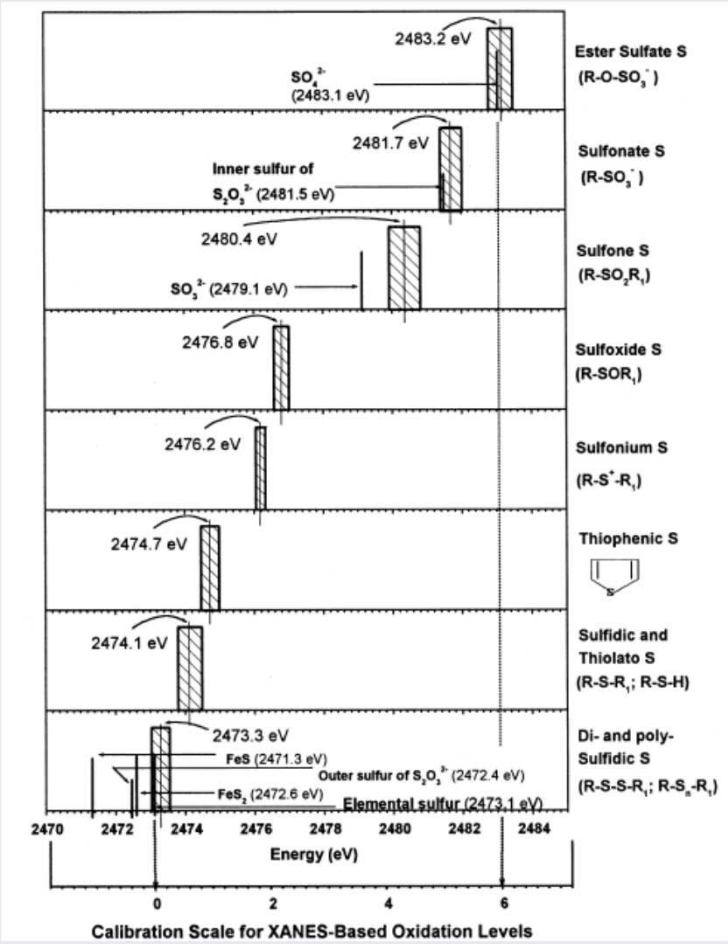
Sulphur K edges in organic compounds having different functionalities

Edge shape = chemical environment

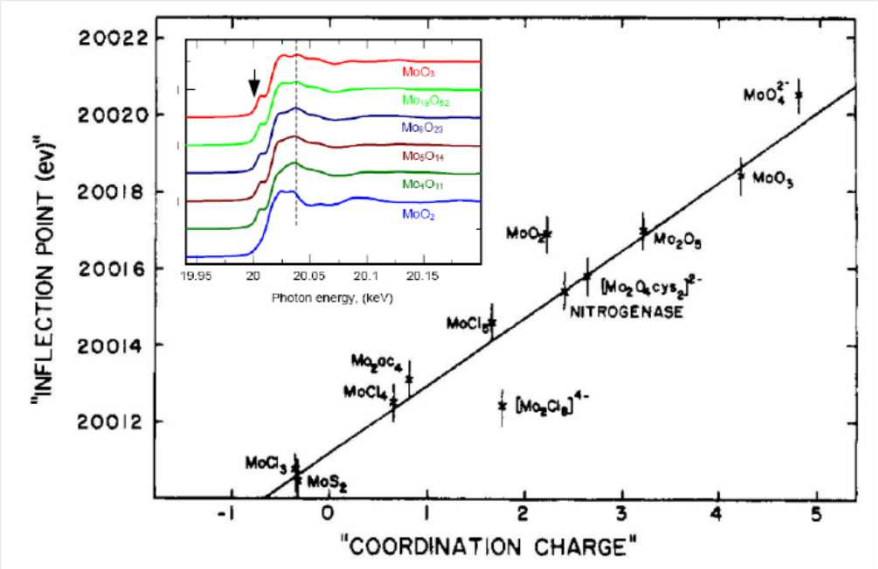


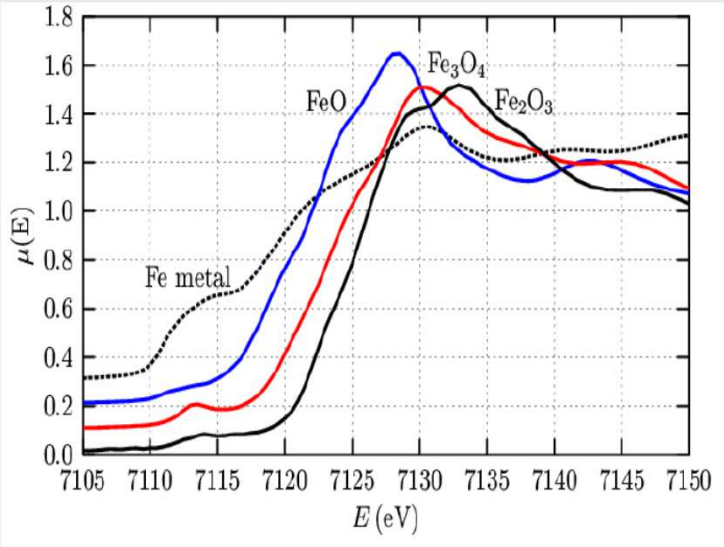
A. Vairavamurthy / Spectrochimica Acta Part A 54 (1998) 2009–2017

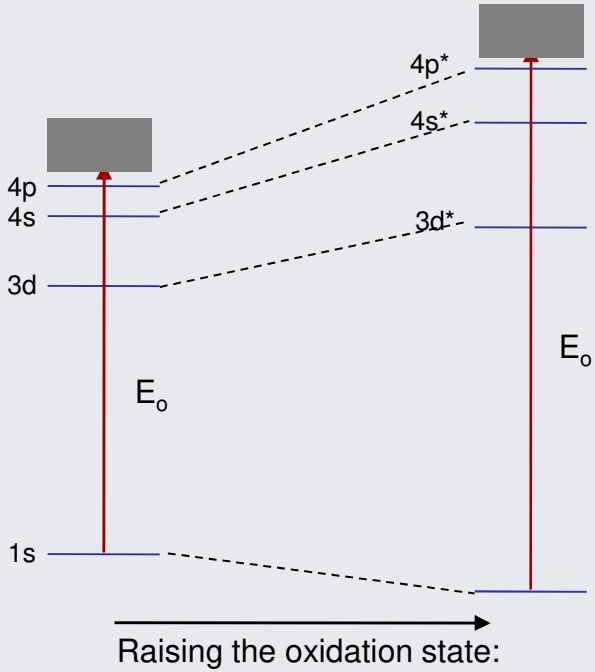
Chemical shift = oxidation state



The chemical shift reveals the absorber oxidation state...







shorter bonds (Coulomb)

↓

destabilization of antibonding levels

decreases the screening

↓

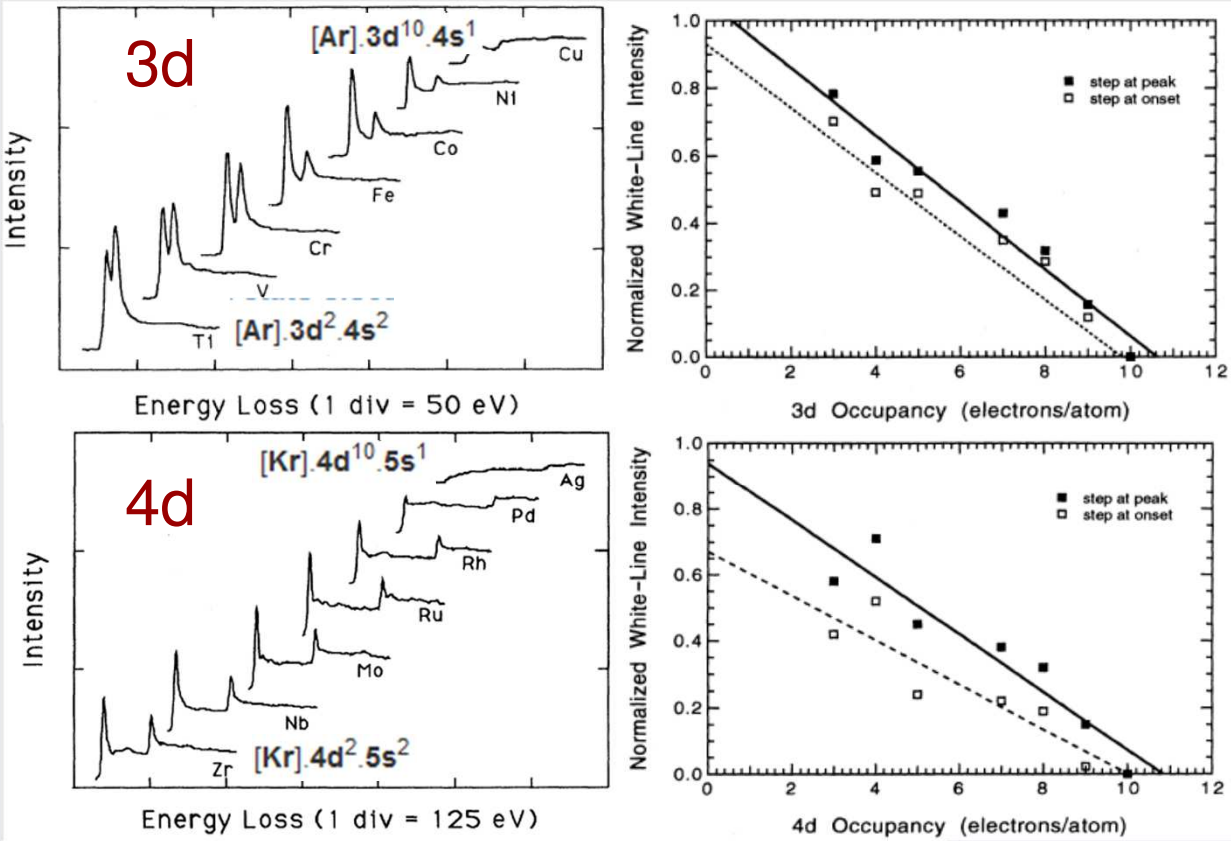
stabilization of core level

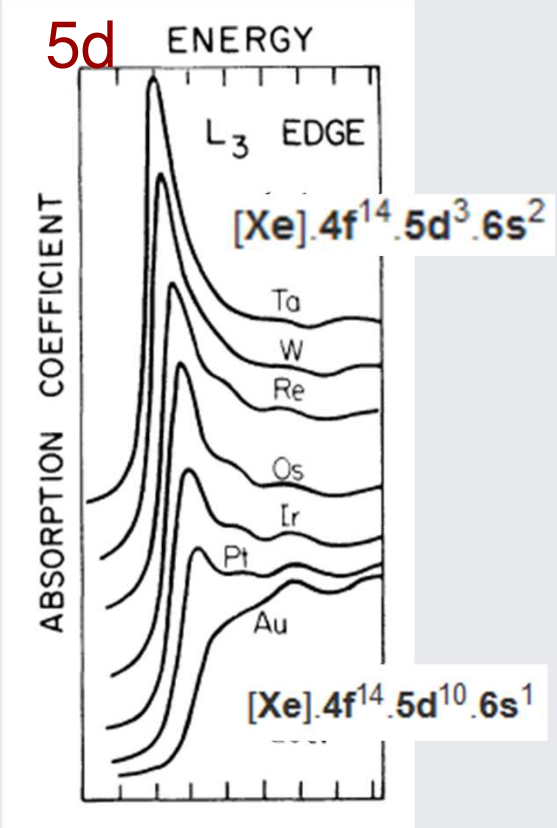
Higher oxidation state

=

High energy shift of the resonances

$L_{2,3}$ edge white lines: a probe for occupancy of d band in nd (n=3, 4, 5) elements

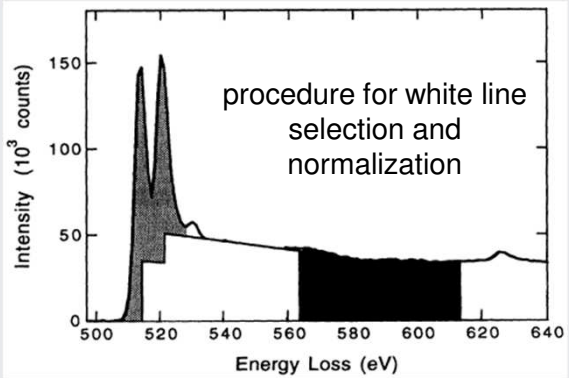




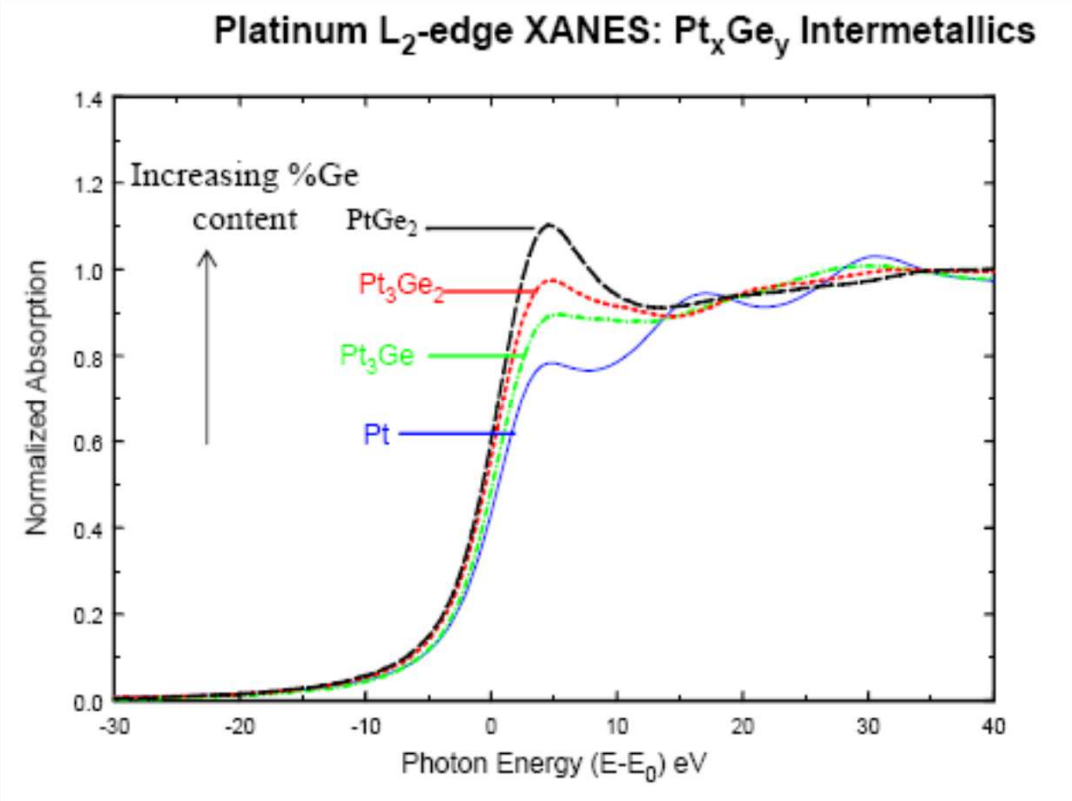
PHYSICAL REVIEW B VOLUME 47, NUMBER 14 1 APRIL 1993-II

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

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

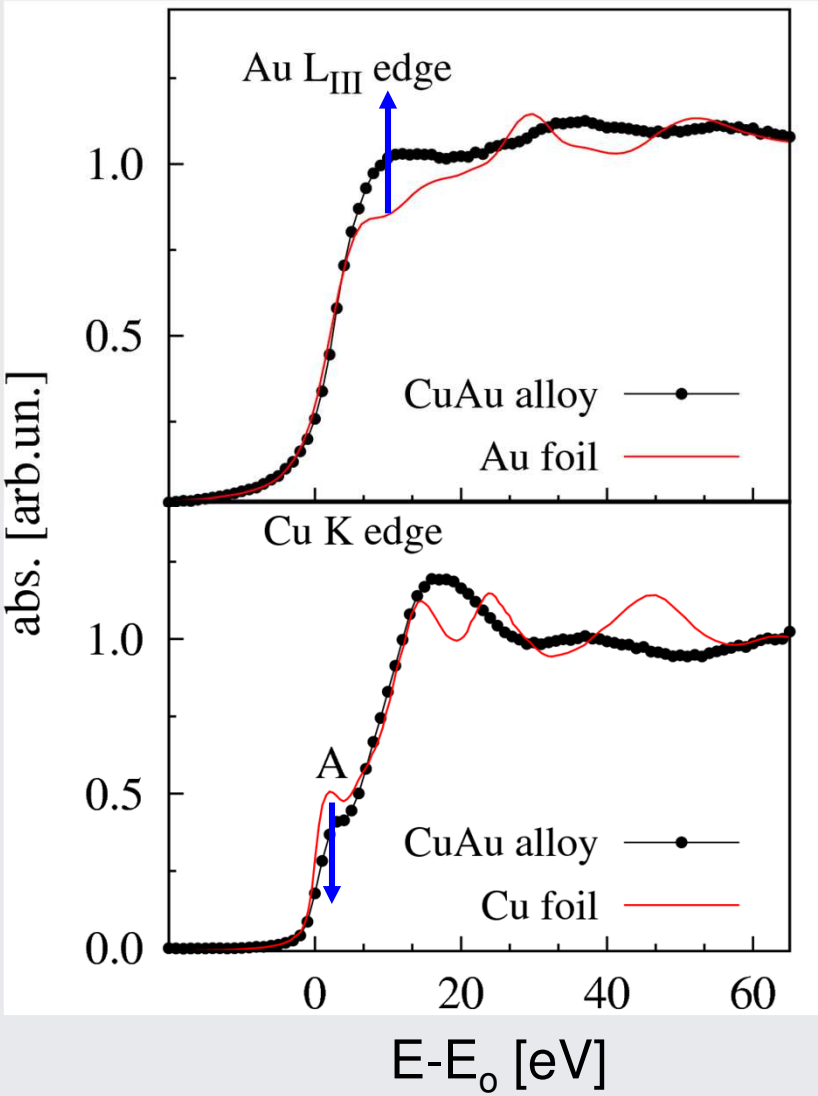


Example: Pt L_2 edge white line in Pt_xGe_y intermetallic compounds



- 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.

Example: Charge transfer in Cu-Au thin film alloy



e^- migrate from Au (increasing density of empty states)

to Cu (decreasing density of empty states)

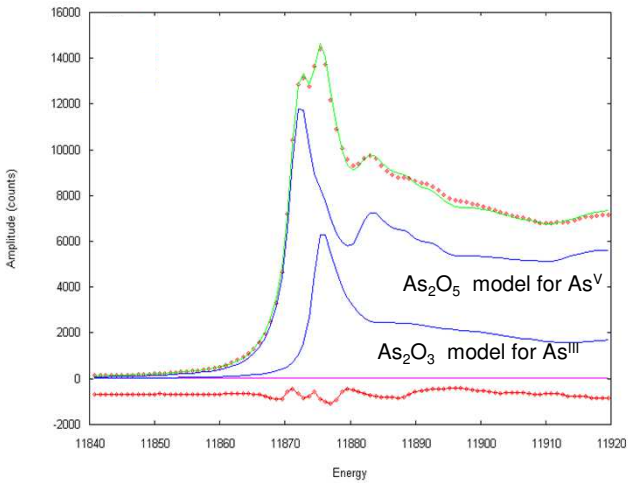
Meneghini et al. Corrosion effects in CuAu thin films (to be published)

Analysis of mixtures: Linear Combination Analysis

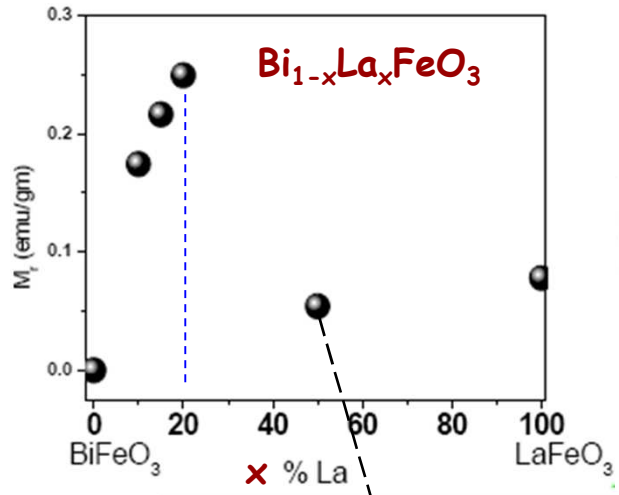
$$\mu^{th} = \sum_j \alpha_j \mu^{ref_j}$$

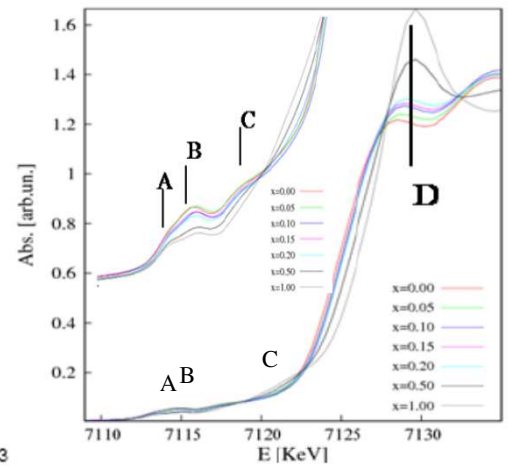
$$R^2 = \sum_i \left(\mu^{exp}(E_i) - \mu^{th}(E_i)\right)^2$$

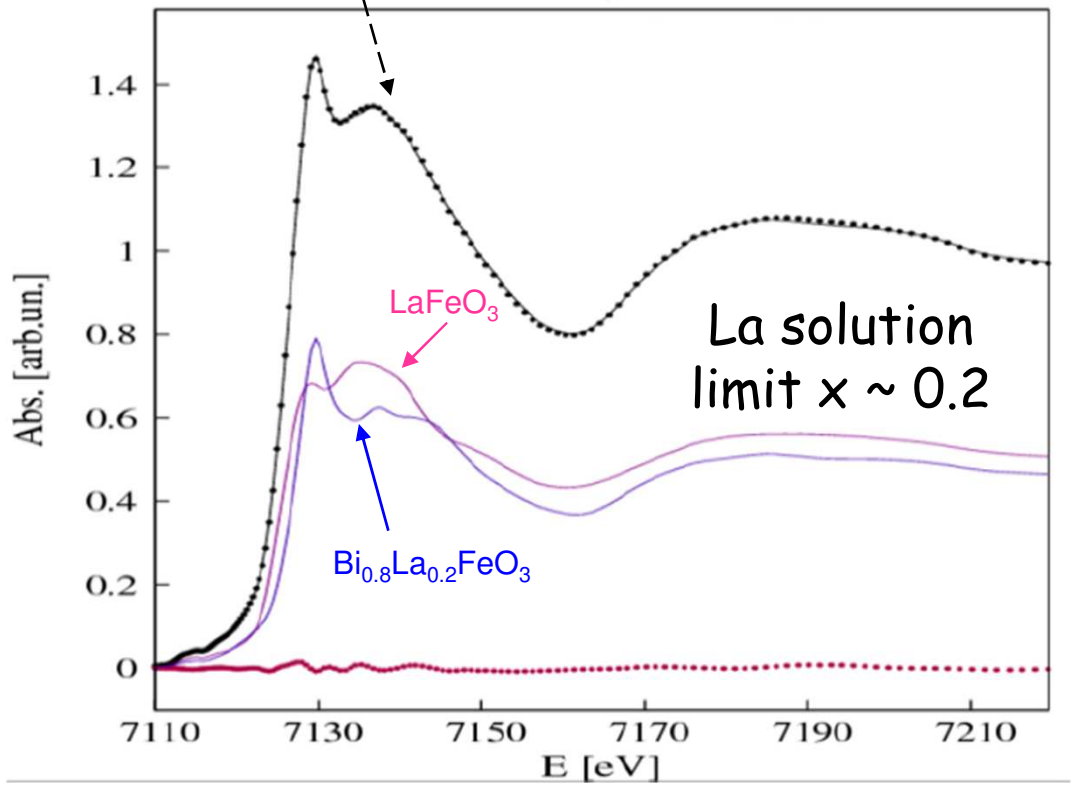
As adsorption in Natural Calcite samples



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





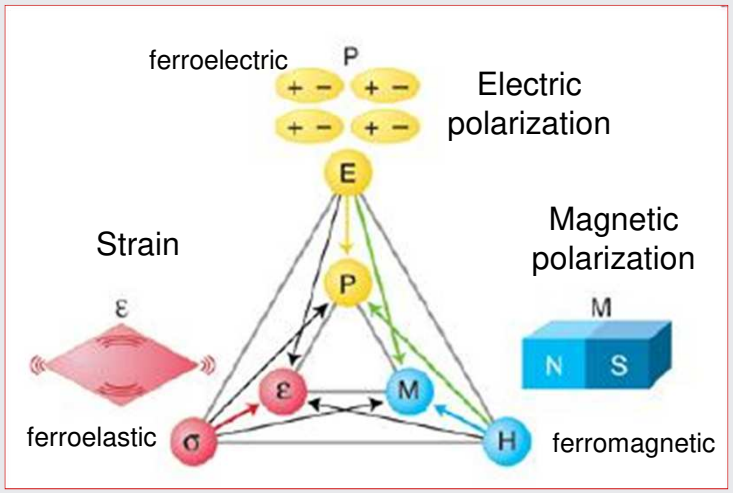


Advanced materials: looking for magneto-electric coupling

Ferromagnetism: a property of certain materials which possess a spontaneous magnetic polarization

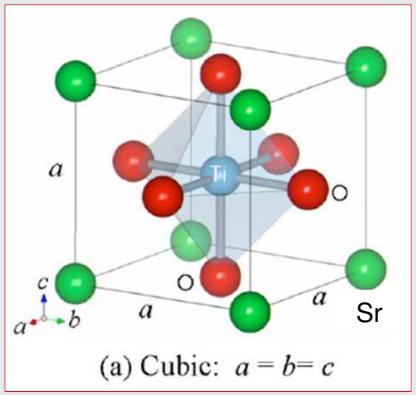
Ferroelectricity: a property of certain materials which possess a spontaneous electric polarization

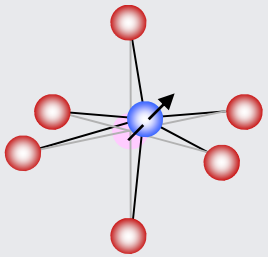
Magneto-electric coupling: magnetic control of ferroelectricity and/or electric control of ferromagnetism may open the way to new devices



Advanced materials: looking for magneto-electric coupling

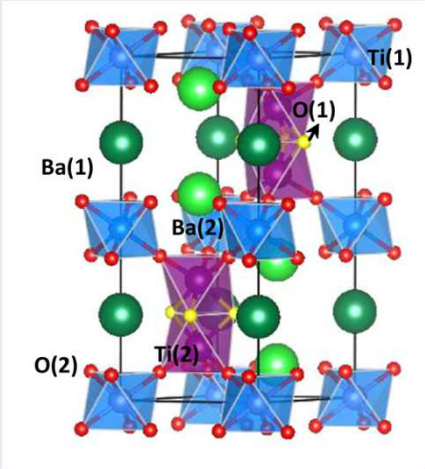
$BaTiO_3$





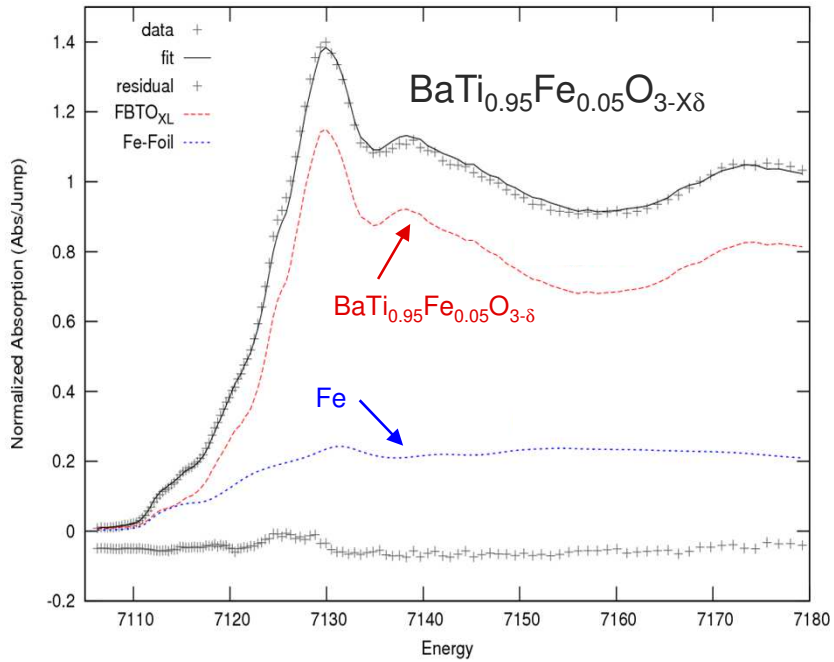
$BaTiO_3$ is **ferroelectric**: off center displacement of Ti^{4+} ions produces a permanent electric dipole in TiO_6 molecules

$BaTiO_{3-\delta}$



doping with magnetic ions (Fe) may provide some magnetoelectric coupling

$BaTi_{0.95}Fe_{0.05}O_{3-\delta}$

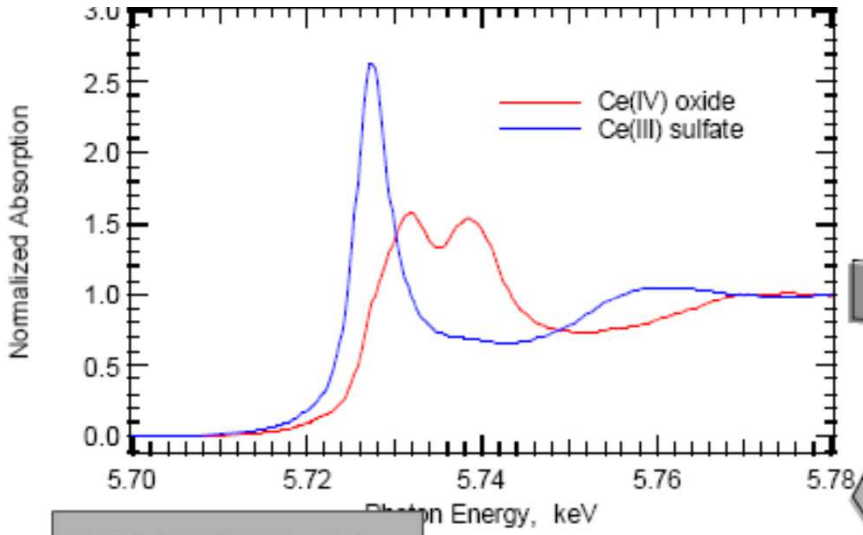


Large Oxygen vacancies causes the Fe ions segregating as metallic Fe^0 phase, the sample is no more homogeneous at the short range scale, wrong magneto-electric understanding

Note: XRD does not show Fe crystalline phase!

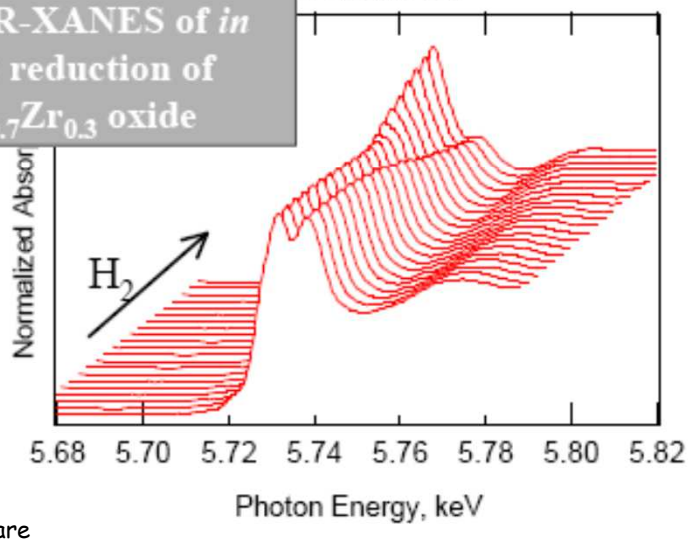
T. Chakraborty, C. Meneghini, G. Aquilanti, S. Ray, J. Phys.: Condens. Matter 25 (2013) 23600
T. Chakraborty, C. Meneghini, G. Aquilanti, S. Ray, Advanced Functional Materials, Submitted

LCA-Catalysis

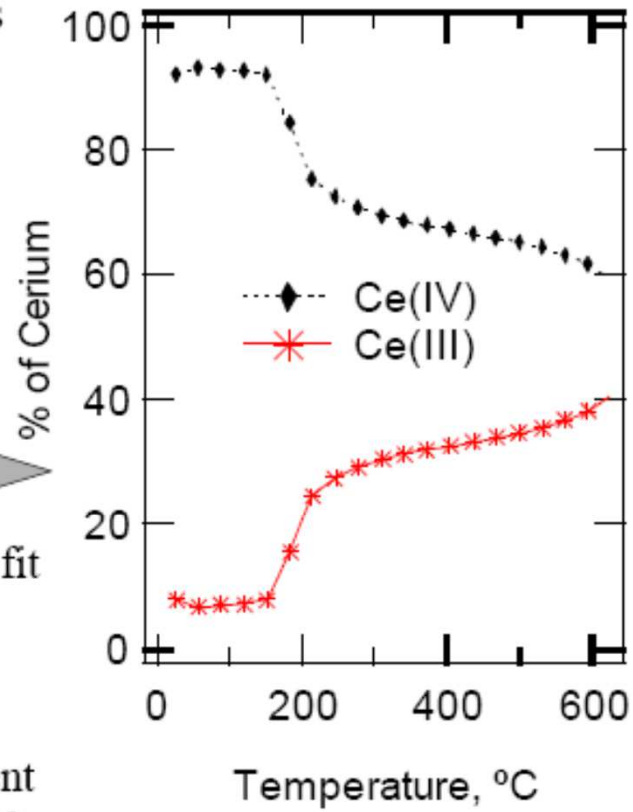


Fit experimental data to linear combination of known reference compounds

TPR-XANES of *in situ* reduction of $Ce_{0.7}Zr_{0.3}$ oxide



LC-XANES fit to determine amount of Ce(III) and Ce(IV) present as function of temperature

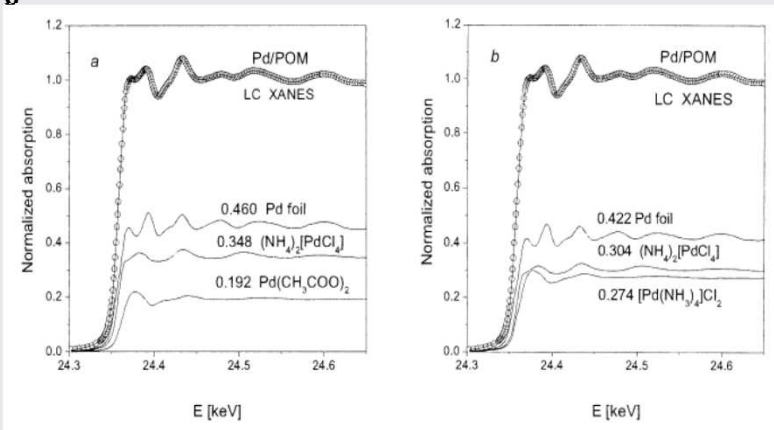


Simon R. Bare

Principal component analysis (PCA)

*Determination of molybdenum surface environment of molybdenum/titania catalysts by EXAFS, XANES and PCA. Mikrochimica Acta 109 (1992) 281.

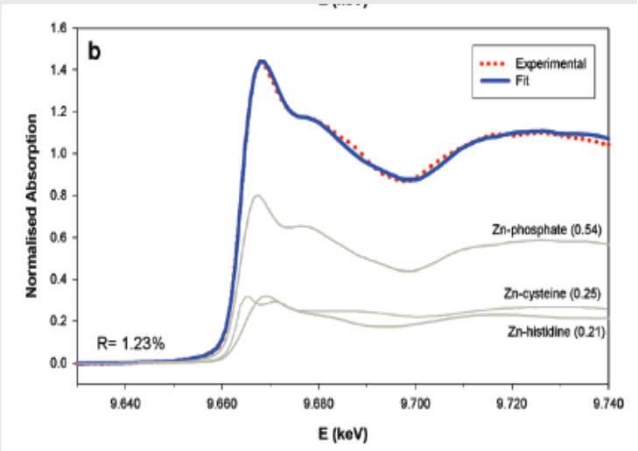
PCA, based on linear algebra e statistical methods, is widely used in pattern recognition problems. Each reference spectrum (component) represent a vector, the data are reproduced by vectorial sum. The algorithms automatically determine (statistics) the relevant components (principal) out a given ensamble and reject the others



J.W. Sobczak J. of All. and Comp. 362 (2004) 162

Local structure of a Pd-doped polymer

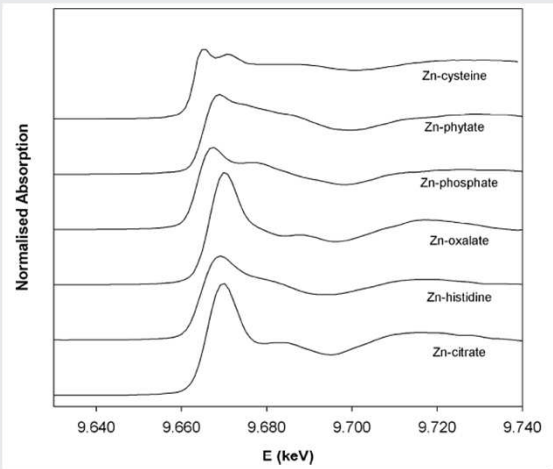
Automatic procedure to select principal components on the basis of their statistical relevance



Warning

- How many standards are necessary?
- Which standards are required?
- Which standards are unphysical?
- Is the final fit reasonable?

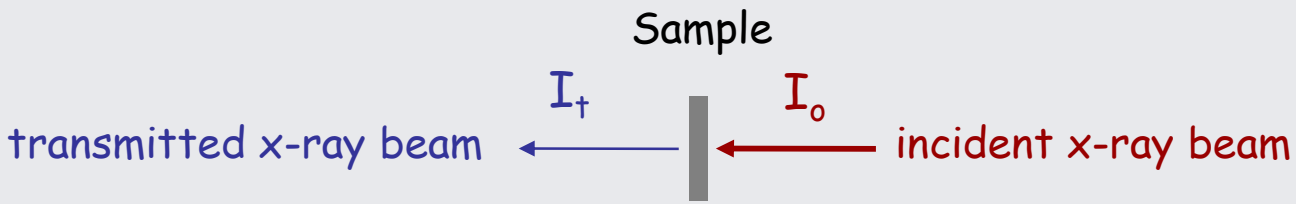
- Use all the a-priori knowledge on the sample (physics, chemistry, etc…)
- Check carefully the results



J. Agric. Food Chem. **2008**, *56*, 3222-3231

XA(NE)S data collection is conceptually simple

Transmission geometry



$$I_t = I_o e^{-\mu \cdot x}$$

μ = Linear absorption coefficient

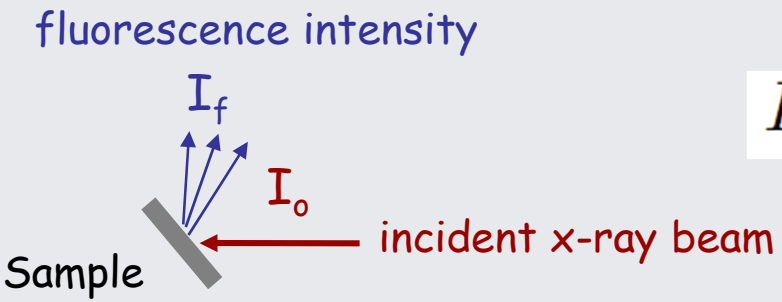
$$\mu x = \ln \frac{I_o}{I_t}$$

Fluorescence geometry

$$I_f \propto I_o - I_t = I_o(1 - e^{-\mu \cdot x})$$

$$\mu \cdot x \ll 1$$

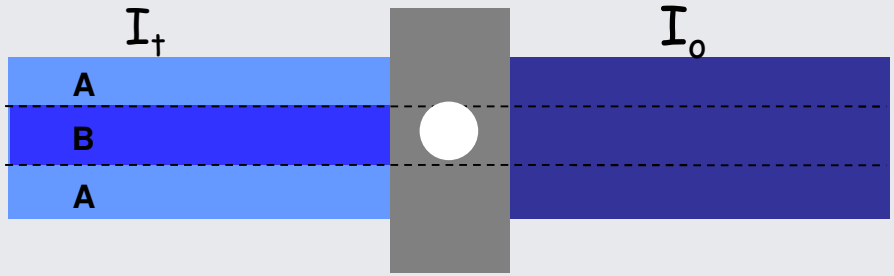
$$I_f \simeq I_o \mu \cdot x$$



$$\mu x \simeq \frac{I_f}{I_o}$$

… but: some *caveat* on data collection

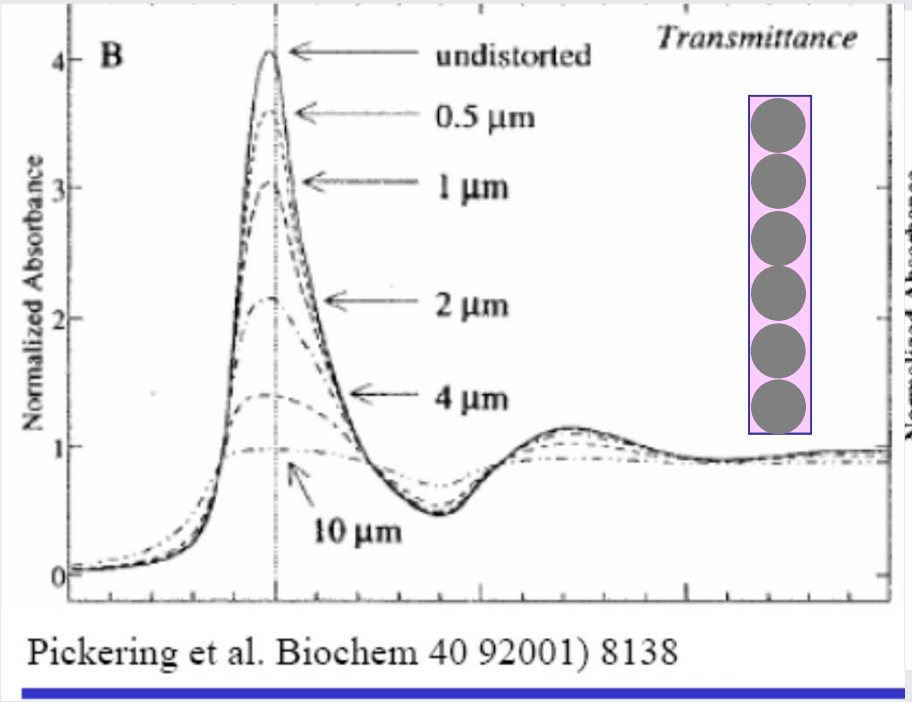
Transmission geometry: inhomogeneous samples (i.e. holes) may determine severe distortions of the XA(NE)S spectra



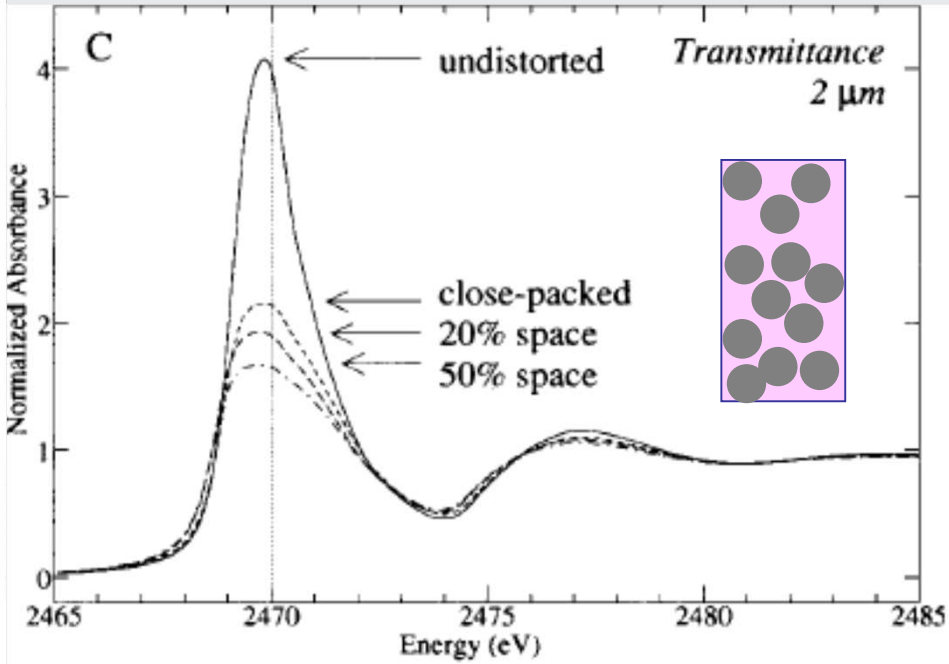
$$I_t = I_o(y_A \cdot e^{-\mu_A x} + y_B \cdot e^{-\mu_B x})$$

! $$\ln \frac{I_o}{I_t} = \ln(y_A \cdot e^{-\mu_A x} + y_B \cdot e^{-\mu_B x})$$!

S- K edge calculated for a layer of spheres

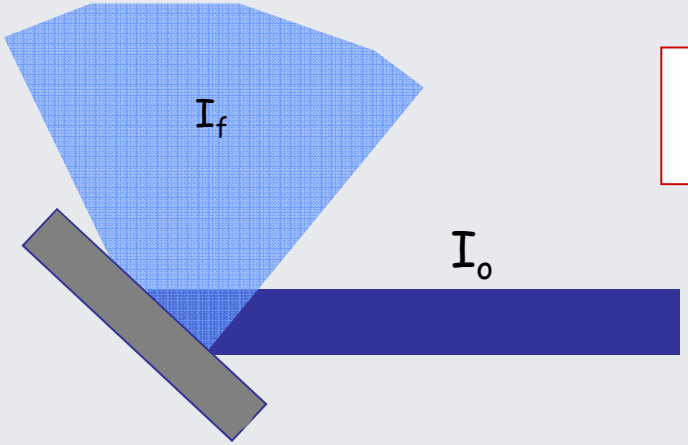


S- K edge calculated for an ensemble of spheres



some *caveat* on data collection

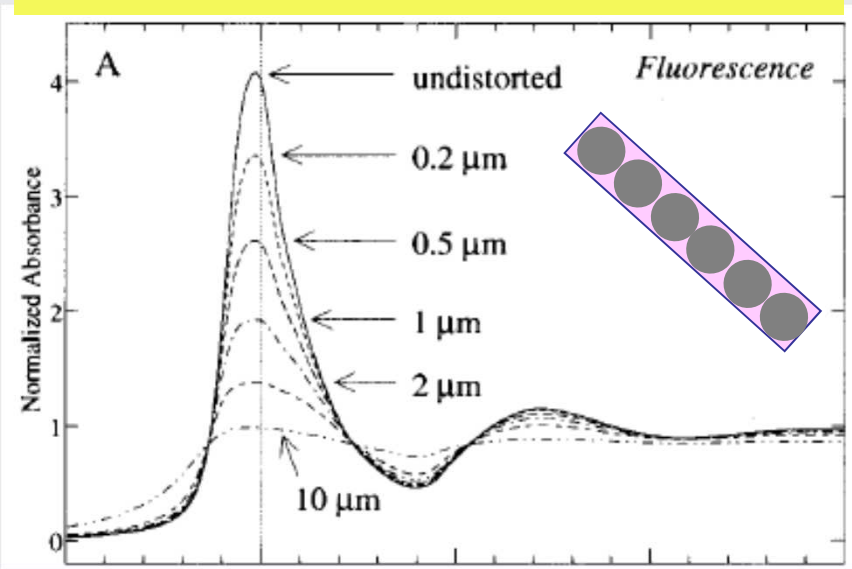
Fluorescence geometry: re-absorption and detector linearity may determine severe distortions of the XA(NE)S spectra

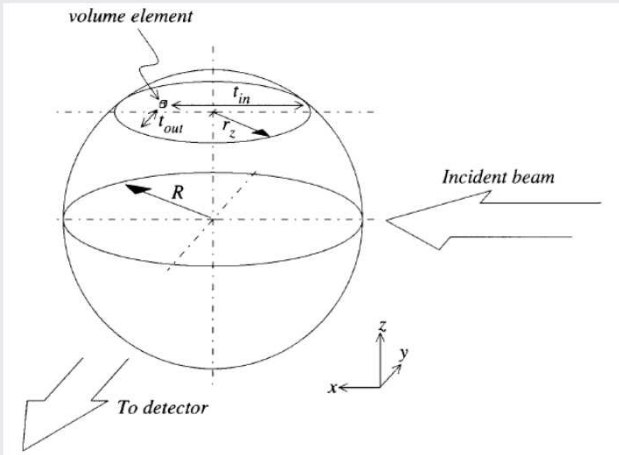


$$I_f \propto I_o - I_t = I_o(1 - e^{-\mu x}) \simeq I_o \mu x$$

$\mu x << 1$

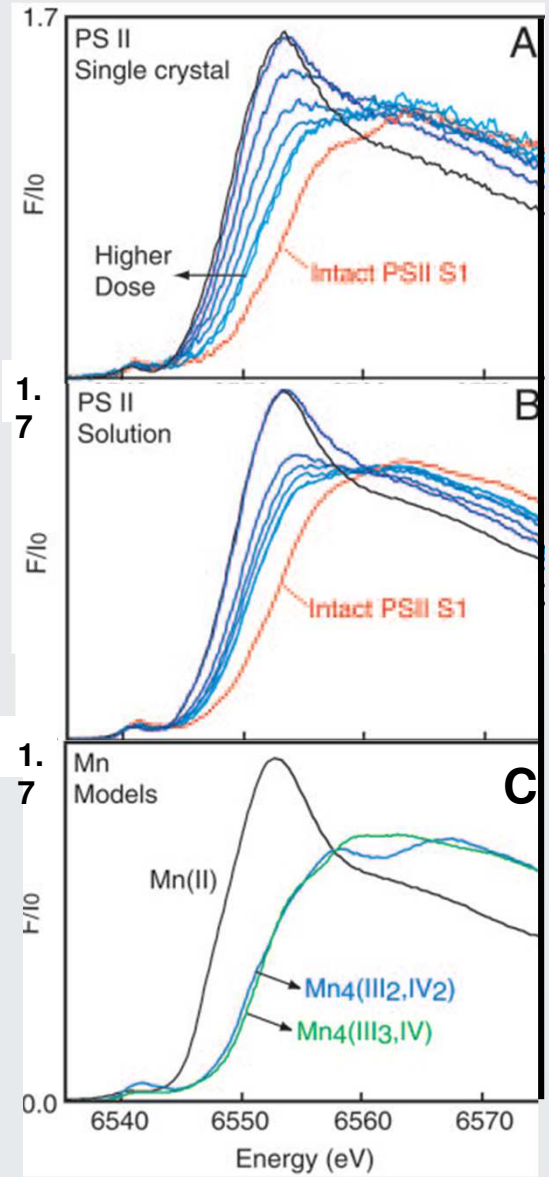
effect of particle size (spheres) on I_f





some caveat on data collection

photoreduction on
Mn_4Ca PS(II) complex



Proc. Natl. Acad. Sci. USA **102**, 12047 (2005)

Radiation Damage & photoreduction

R.D. is a function of exposure time/dose, provoke shift of the edge and deformation of XAFS features.

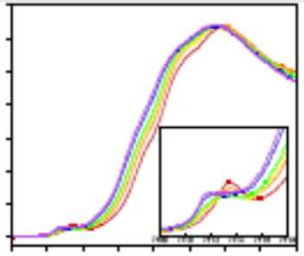
R.D. can be reduced by:

- reducing the x-ray intensity
- reducing the exposure time
- collecting data at low sample temperature

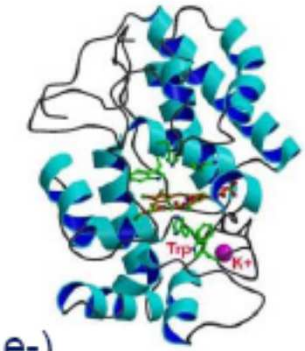
R.D. can be very relevant in biological samples like metalloproteins.

Details about radiation damage and photoreduction can be relevant for reliable protein crystallography

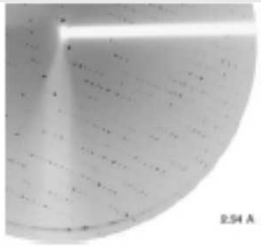
Radiation Damage: XAS and Crystallography



XAS



PX



Visible Effect

- Edge shift (~ 1 eV per e-)
- Shift in EXAFS peak positions

Visible Effect

Loss of diffraction intensity

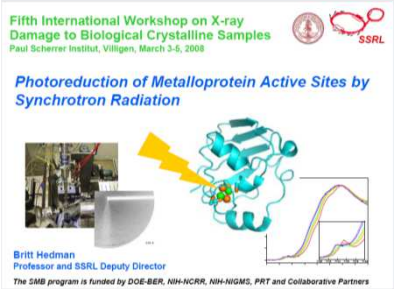
- Increased unit cell volume

Structural Effect

- *Can be monitored over time (repeated single scans)*
- Longer Metal-Ligand bonds and/or increased σ^2 in M-L paths
- Change in site geometry due to irradiation/chemical reaction

Structural Effect

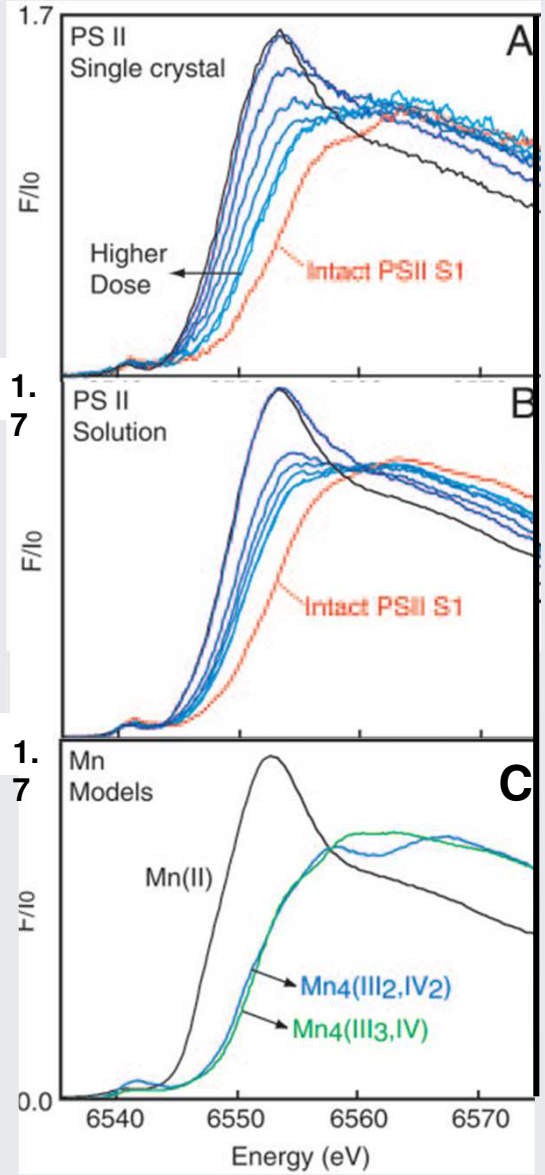
- *Not monitored over time (one cumulative data set)*
- Breakage of selected bonds
- High DW-factors
- Loss of or unexplained density



XAFS can be used to monitor (in situ) photoreduction of metals

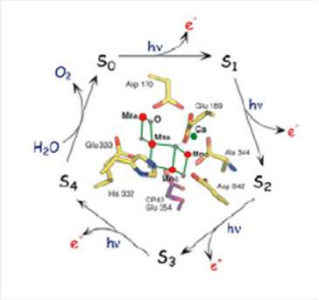
X-ray damage to the Mn_4Ca complex in single crystals of photosystem II: A case study for metalloprotein crystallography

Junko Yano*†‡, Jan Kern‡§, Klaus-Dieter Irrgang§, Matthew J. Latimer¶, Uwe Bergmann¶, Pieter Glatzel‖, Yulia Pushkar*†, Jacek Biesiadka**, Bernhard Loll**, Kenneth Sauer*†, Johannes Messinger†‡‡, Athina Zouni§‡‡, and Vittal K. Yachandra*‡‡



Proc. Natl. Acad. Sci. USA **102**, 12047 (2005)

Photosynthesis uses light energy to **produce O_2 and fix CO_2.** This process generates an aerobic atmosphere and produces a readily usable carbon source.



Photosystem II (PSII) reaction catalyzes the photoinduced oxidation of water so it plays an essential role in maintaining the biosphere

It is of considerable importance to elucidate its catalytic mechanisms, particularly those involved in the water oxidation process.

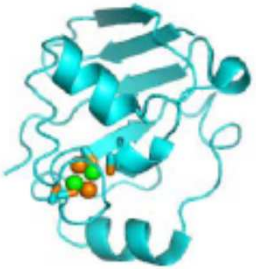
...at present, there are serious discrepancies among the models of the structure of the Mn_4Ca complex in the published x-ray crystallography studies, and there are inconsistencies with x-ray, EPR, and FTIR (...). **This disagreement is predominantly a function of x-ray-induced damage to the catalytic metal site** (...) Therefore, the reported **model of the Mn_4Ca complex** at atomic detail **cannot be based on the diffraction data only** (...).

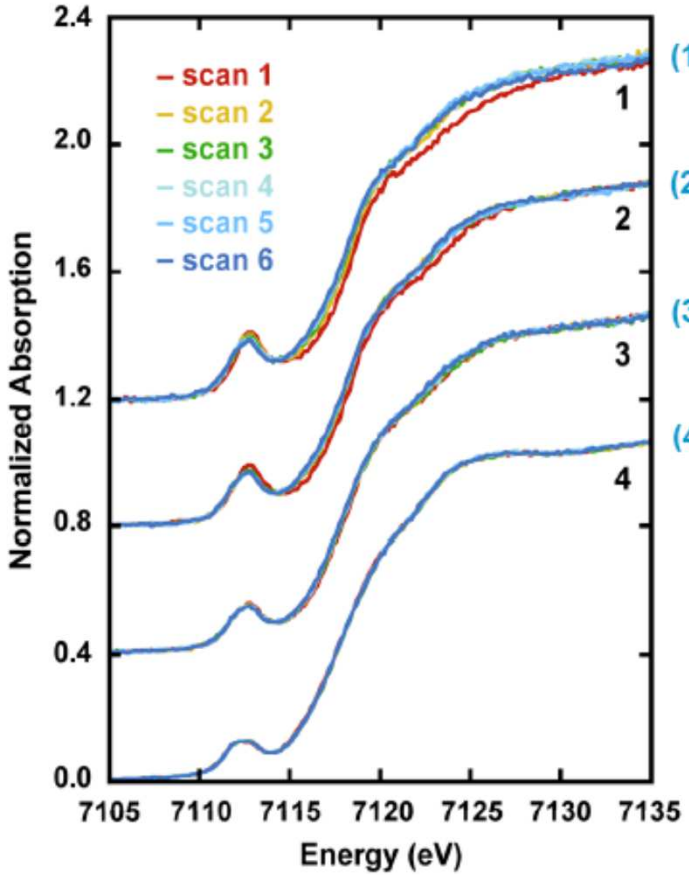
Proc. Natl. Acad. Sci. USA **102**, 12047 (2005)

photo-reduction of Mn ions

Radiation Damage and photoreduction

The PDB lists 40 structures for $[Fe_2S_2]Cys_4$ ferredoxins
8 are described as oxidized, 1 is described as reduced
none include spectroscopy that would verify the redox state!





(1) oxidized crystal at ~ 110 K

Immediate photoreduction during first scan

(2) oxidized crystal at ~ 40 K

Slower photoreduction still during first scan

(3) oxidized solution at 7 K

Still slower photoreduction during first scan

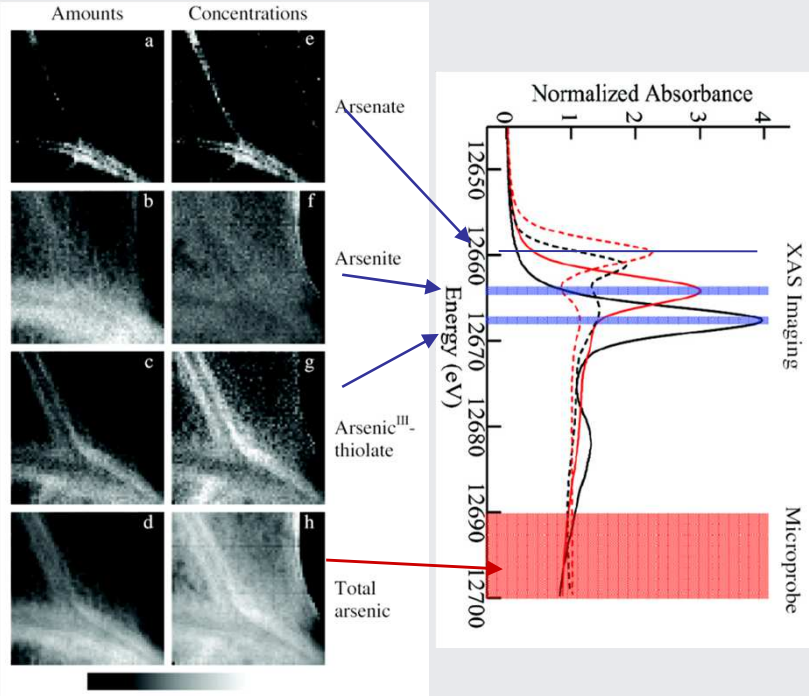
(4) reduced solution at 7 K

Reduced site – no change as expected

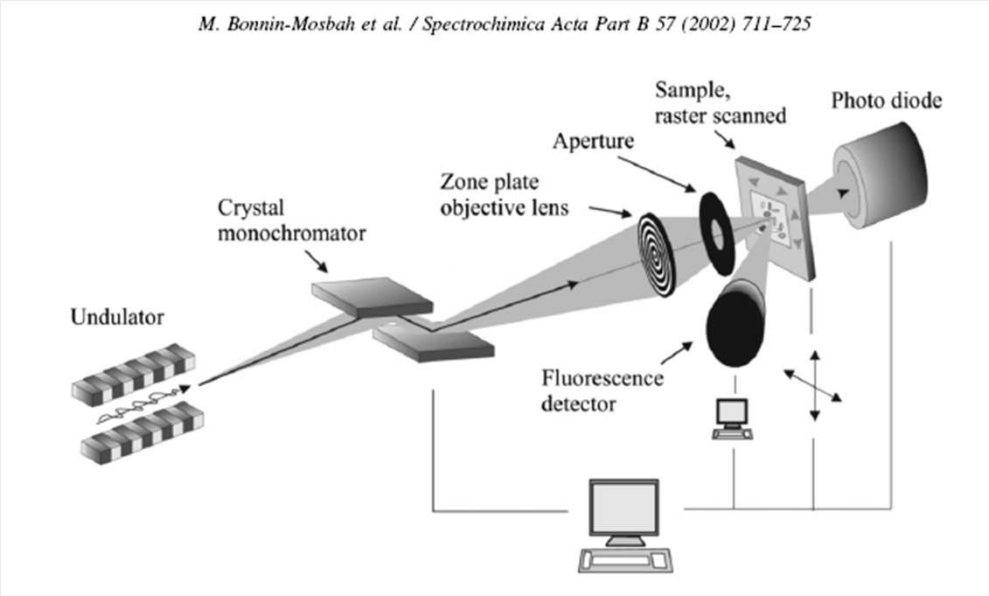
Each set of spectra displays six consecutive scans with a ca. 20 min duration

Other applications of XANES spectroscopy: μ-XANES & mapping

Notice:
μ(n)-XRF= elemental sensitivity
μ(n)-XAS= **elemental sensitivity + chemical speciation**



I. J.Pickering & G. N. George Proc. XAFS13 conference (2006)

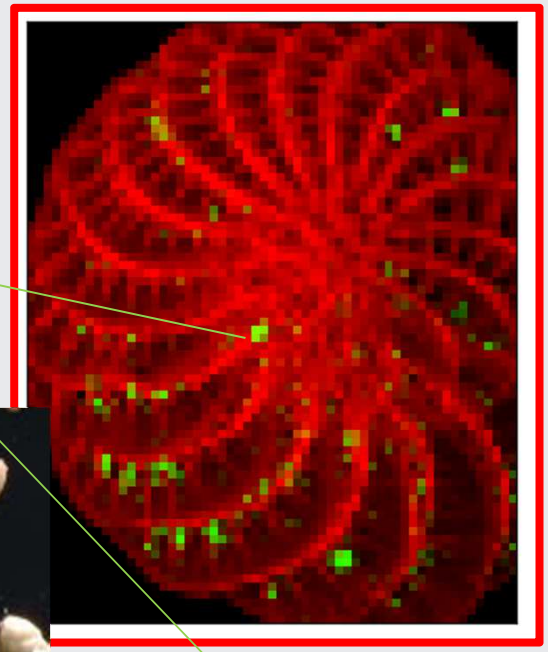


X-ray lenses and zone plates work in a reduced energy window, therefore the EXAFS region is often not accessible to micro and nano probes

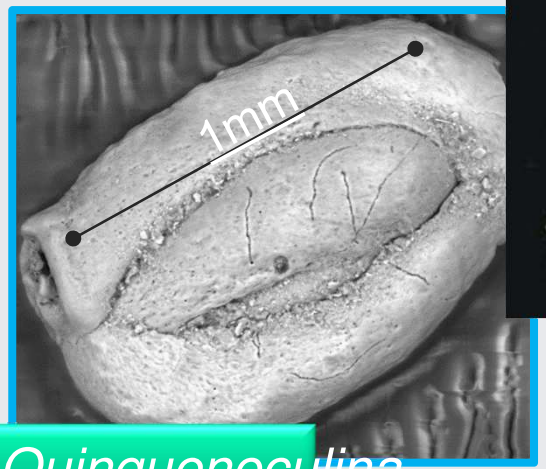
Bio- e Fito-Remediation or:
Plants and (micro-)organisms employed to regulate pollutant mobility (i.e. heavy metals) within the ecosystem and environment

Elphidium

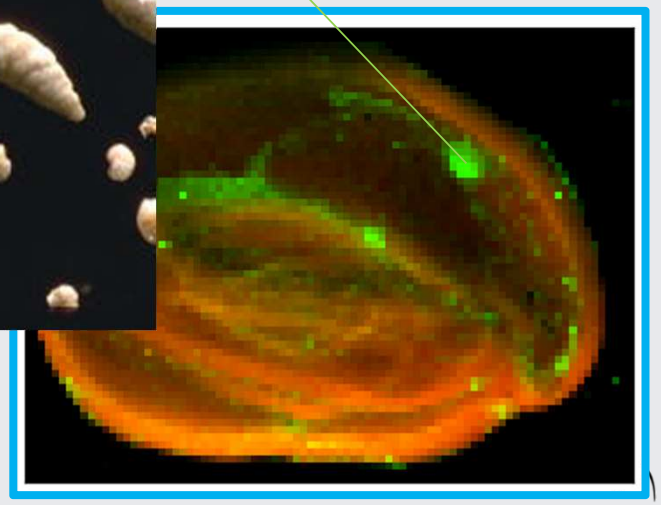
μ-XANES & mapping



Foraminiferi



Quinquenoculina

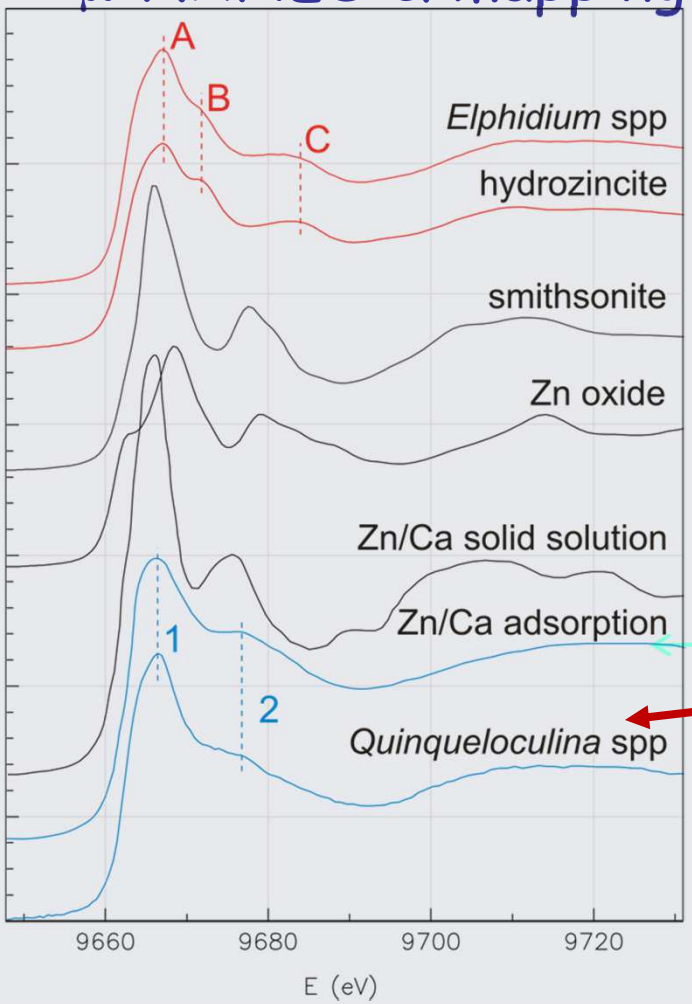


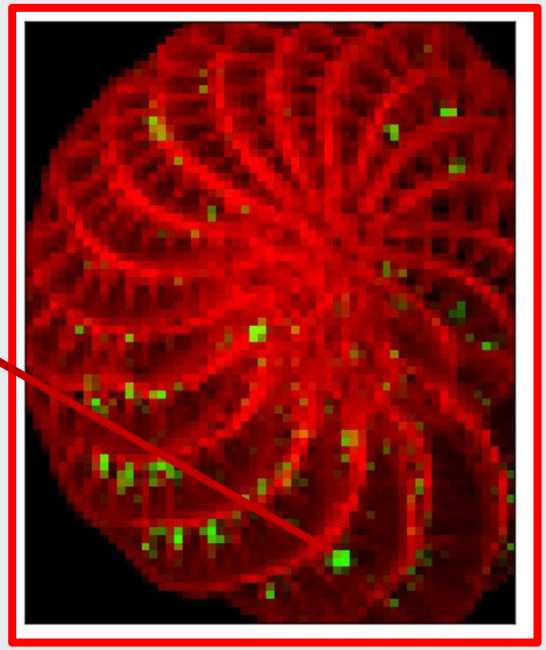
G. De Giudici, D. Medas, P. Lattanzi, C. Meneghini, et al. to be submitted (Scienze)

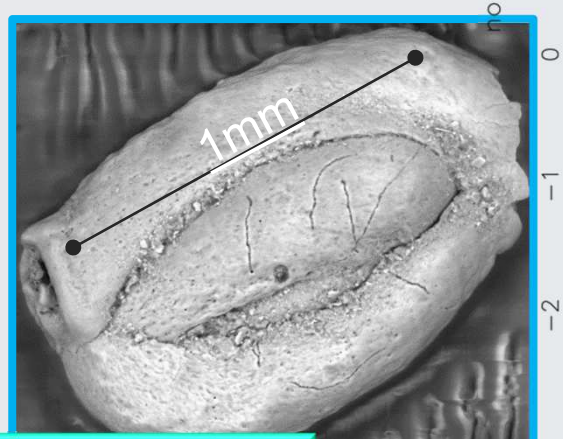
Bio- e Fito-Remediation or:
Plants and (micro-)organisms employed to regulate pollutant mobility (i.e. heavy metals) within the ecosystem and environment

Elphidium

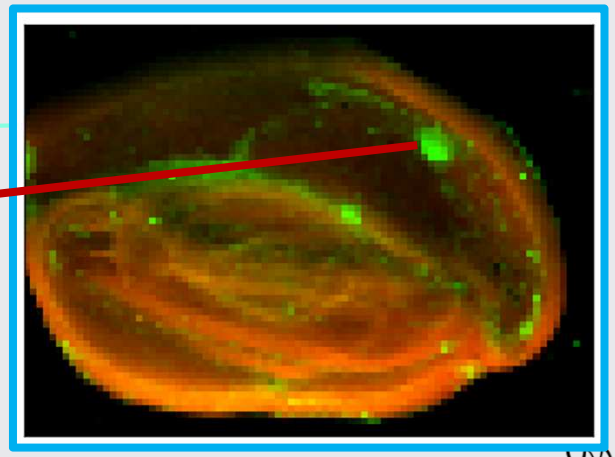
μ-XANES & mapping







Quinquenoculina



G. De Giudici, D. Medas, P. Lattanzi, C. Meneghini, et al. to be submitted (Scienze)

Time resolved XA(NE)S: experimental set-up

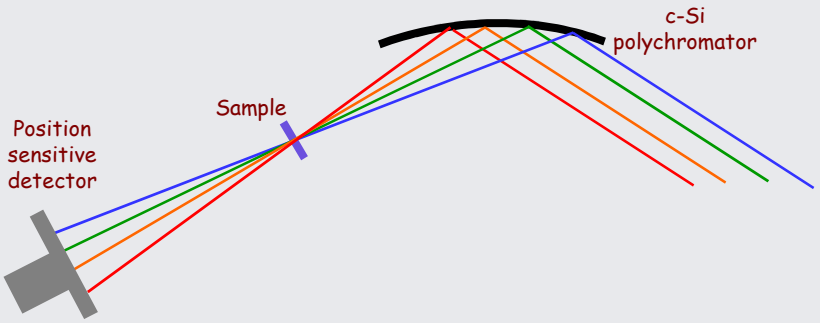
Quick XAFS

$\Delta t = 10\text{-}10^2 s$

any data collection geometry

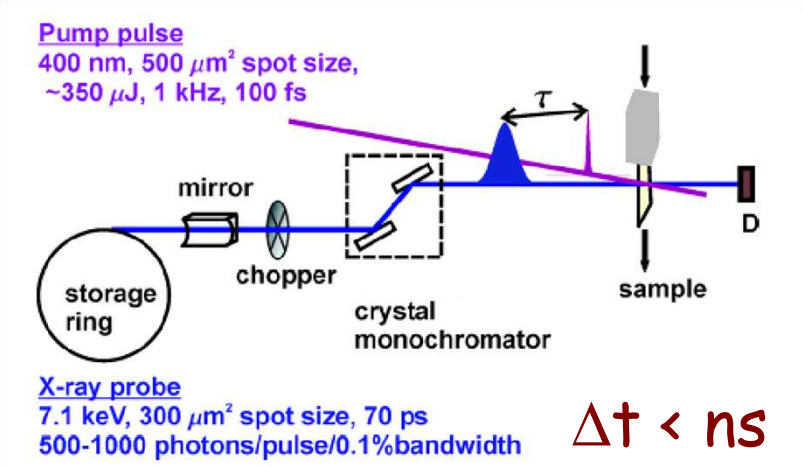
Dispersive XAFS

$\Delta t = 10^{-3} - 1\ s$

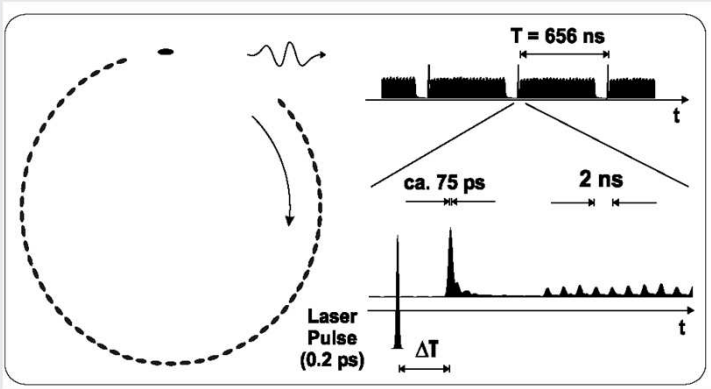


Transmission geometry

Pump probe

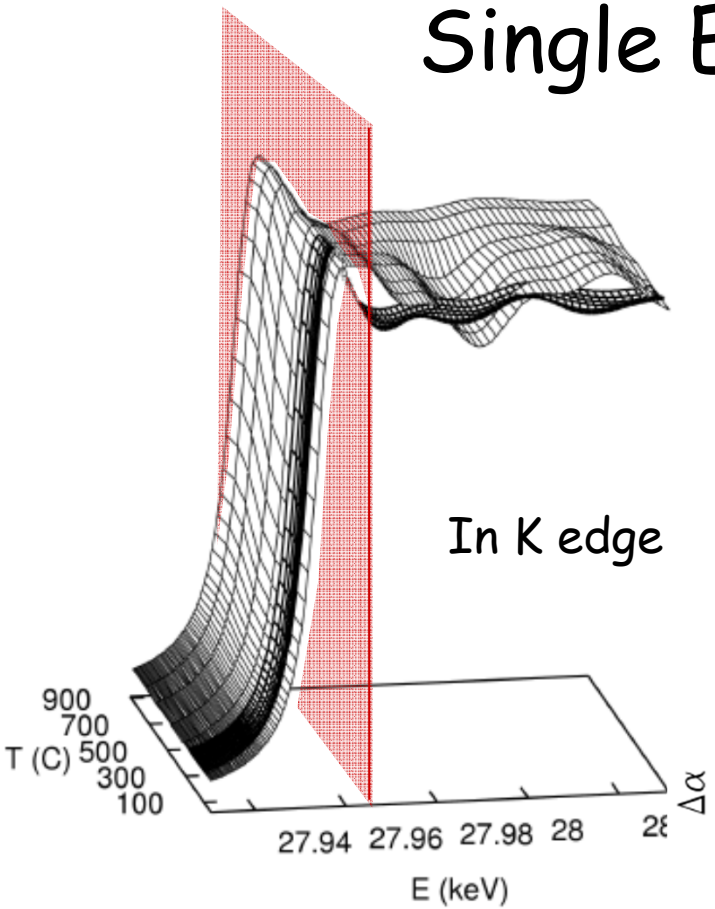


$\Delta t < ns$

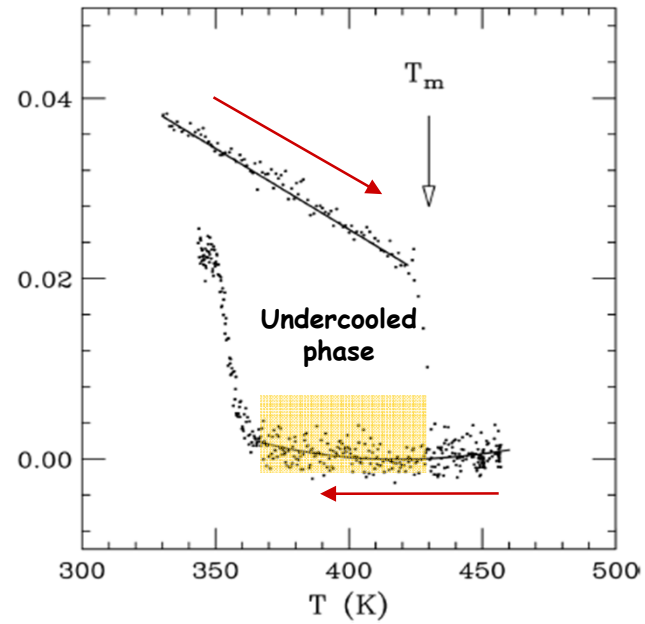


Time resolved XAS

Single Energy - XAS

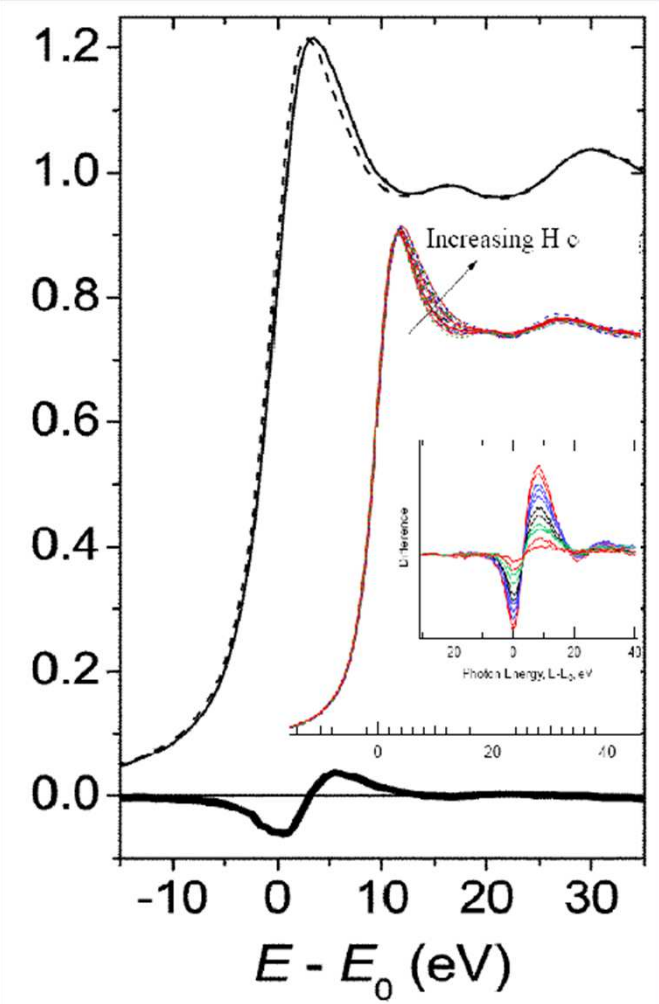


Melting of In μ-particles and structure of undercooled In phase



A. Filipponi et al. J. Sinchr. Rad. 8, 81 (2001)

Time resolved & light elements XAS



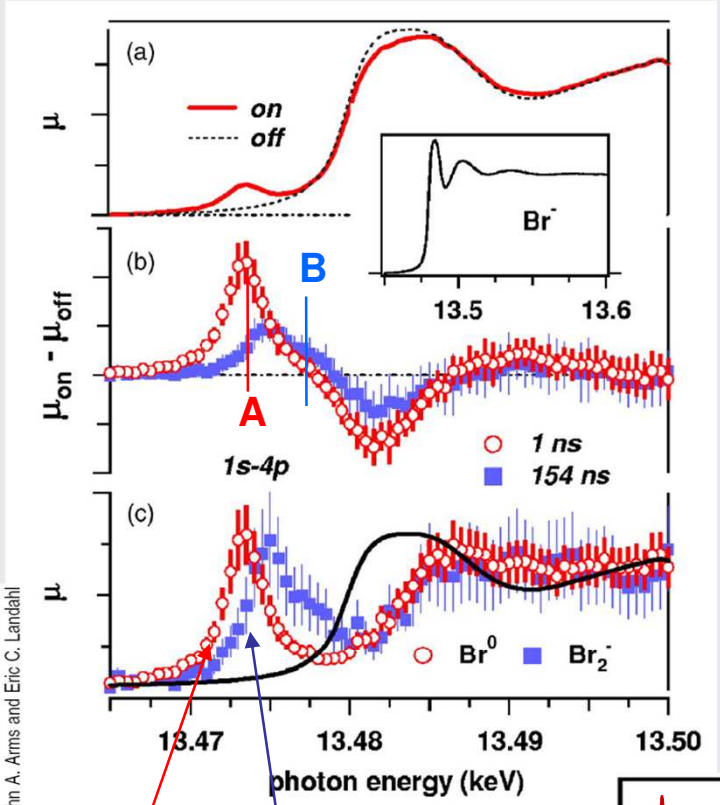
The Effect of H coverage on Pt nanoparticles:

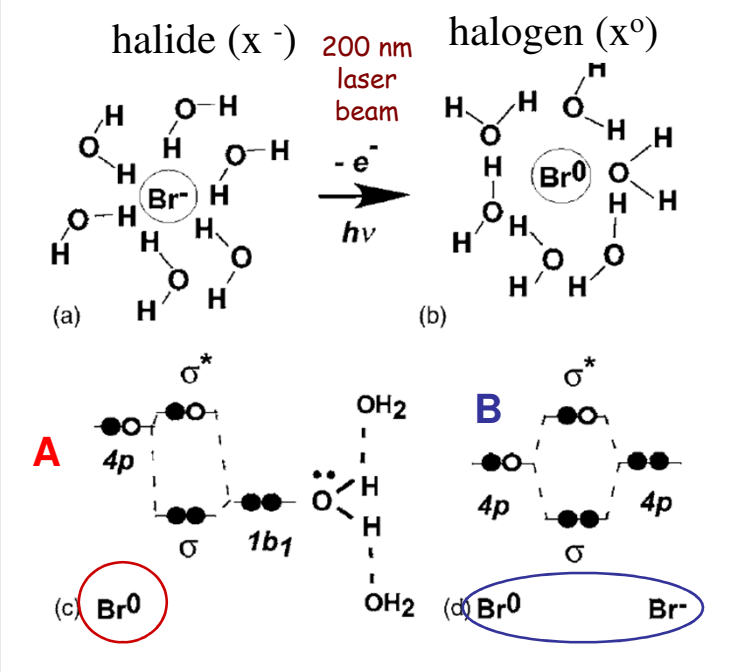
H is notably weakly visible to x-ray

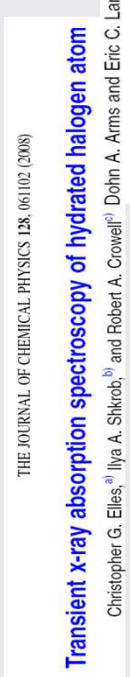
but can be evident in the XANES region

At the Pt L_{III} edge the effect of H is evident and can be followed in-situ to monitor the catalytic activity of Pt clusters as a function of environmental parameters.

Example: transient states of photoexcited hydrated atoms Δt ~1 ns

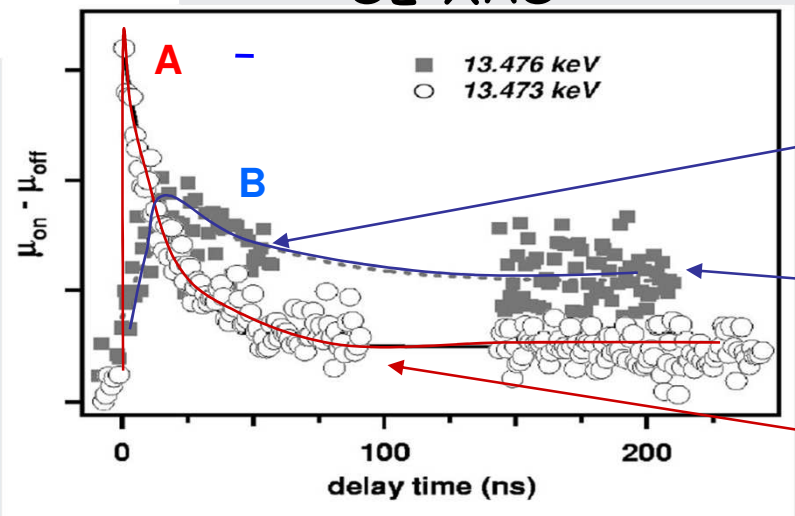






Br_0 Br_2^-

SE-XAS

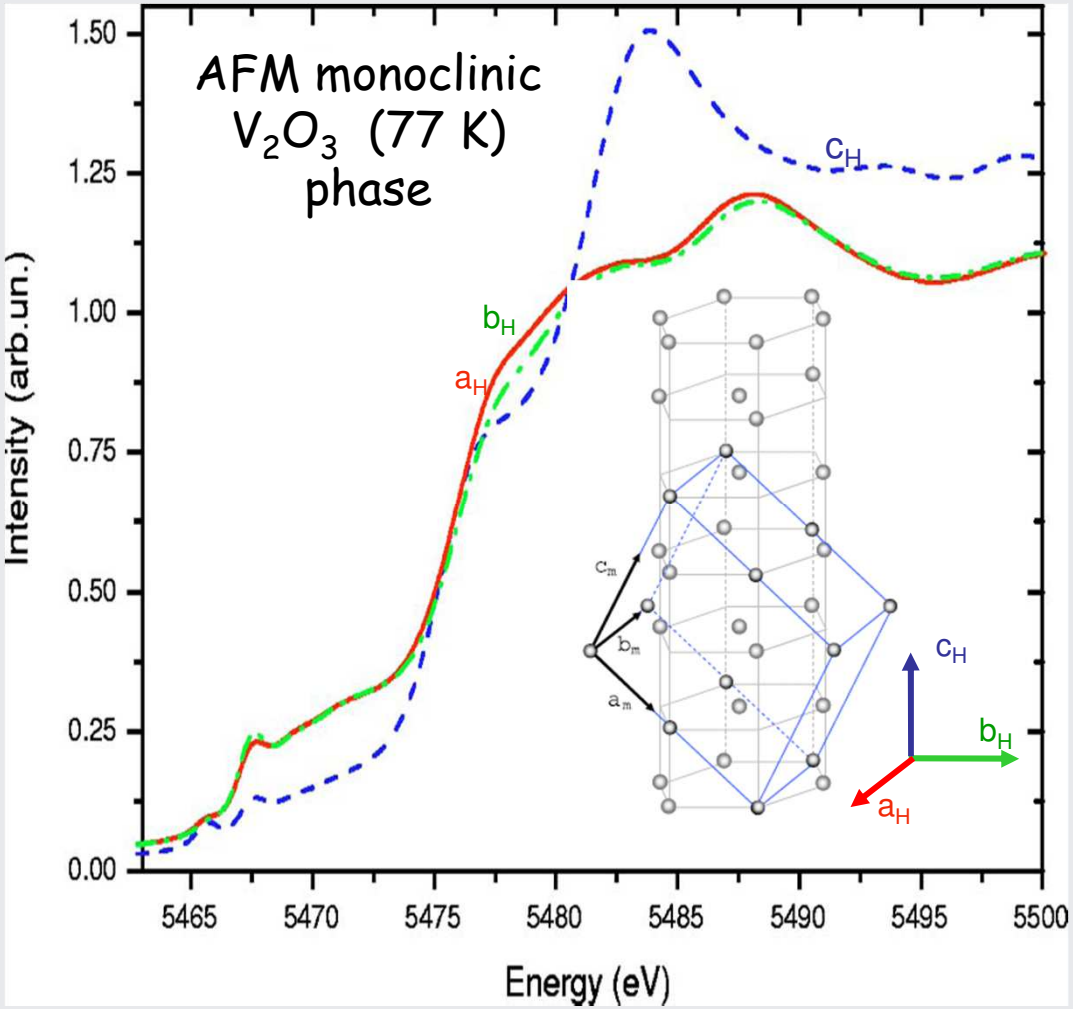


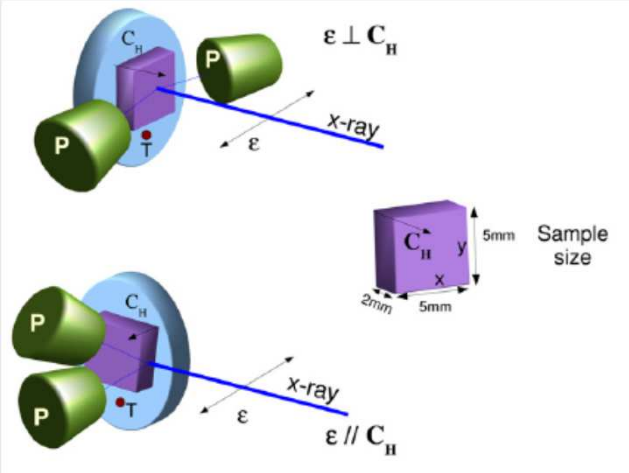
production of Br_2 (Δt ~10 ns)

Br_2 molecules survive after Δt >150 ns

Reaction with water (Δt ~ 50 ns)

Polarized XANES: directional probe for not isotropic structures

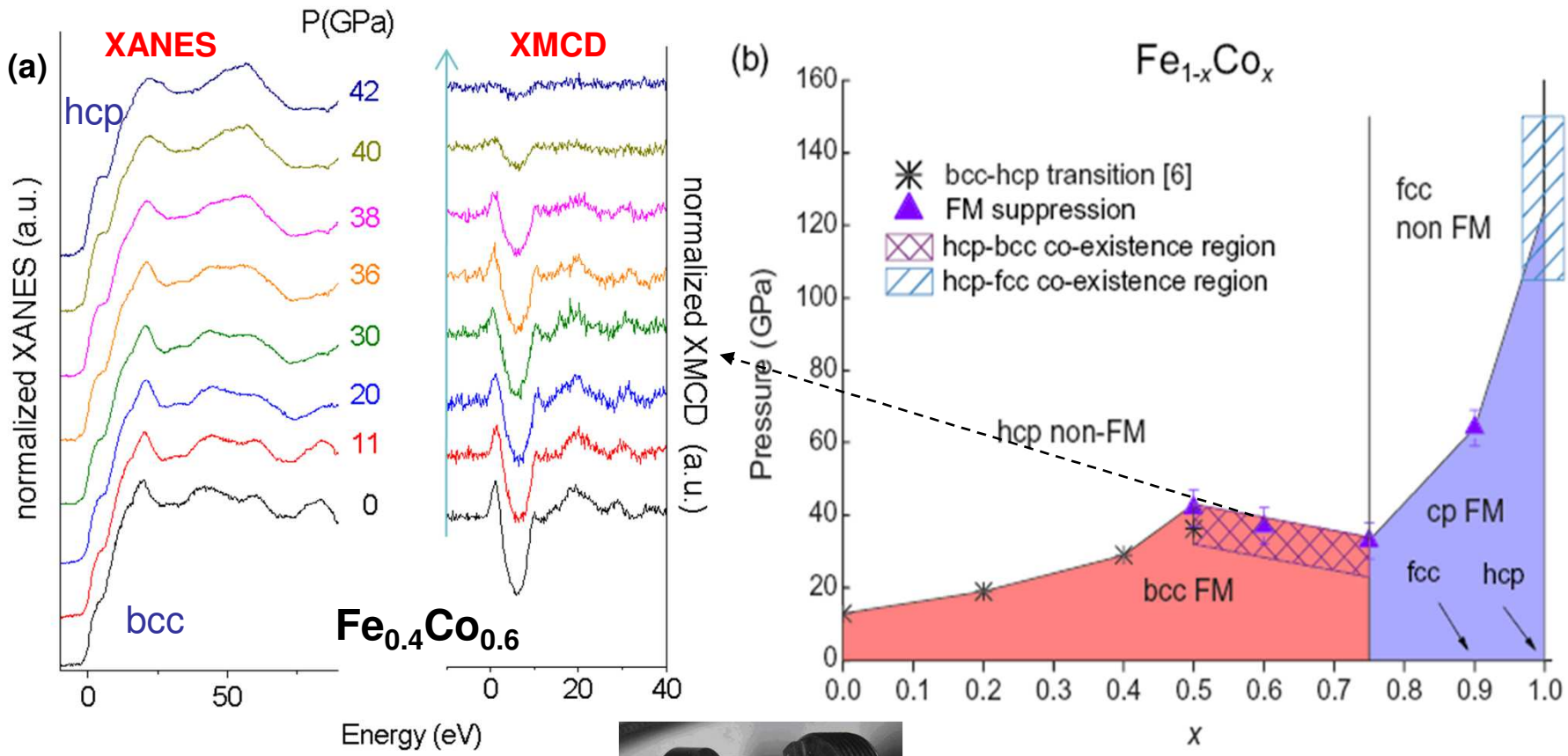




Structural dichroism (absent in hexagonal HT phase) is the fingerprint of monoclinic distortion

XMCD-XANES extreme condition studies

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



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

Thanks for your attention