

# Data analysis of XAFS data

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2. [From XAS to XAFS: data treatment procedures](#)
3. [Training: EXAFS data refinement](#)
4. [\*\*Introduction to XANES\*\*](#)
5. [Training: XANES data analysis](#)

<https://tinyurl.com/SRSelettra2021>

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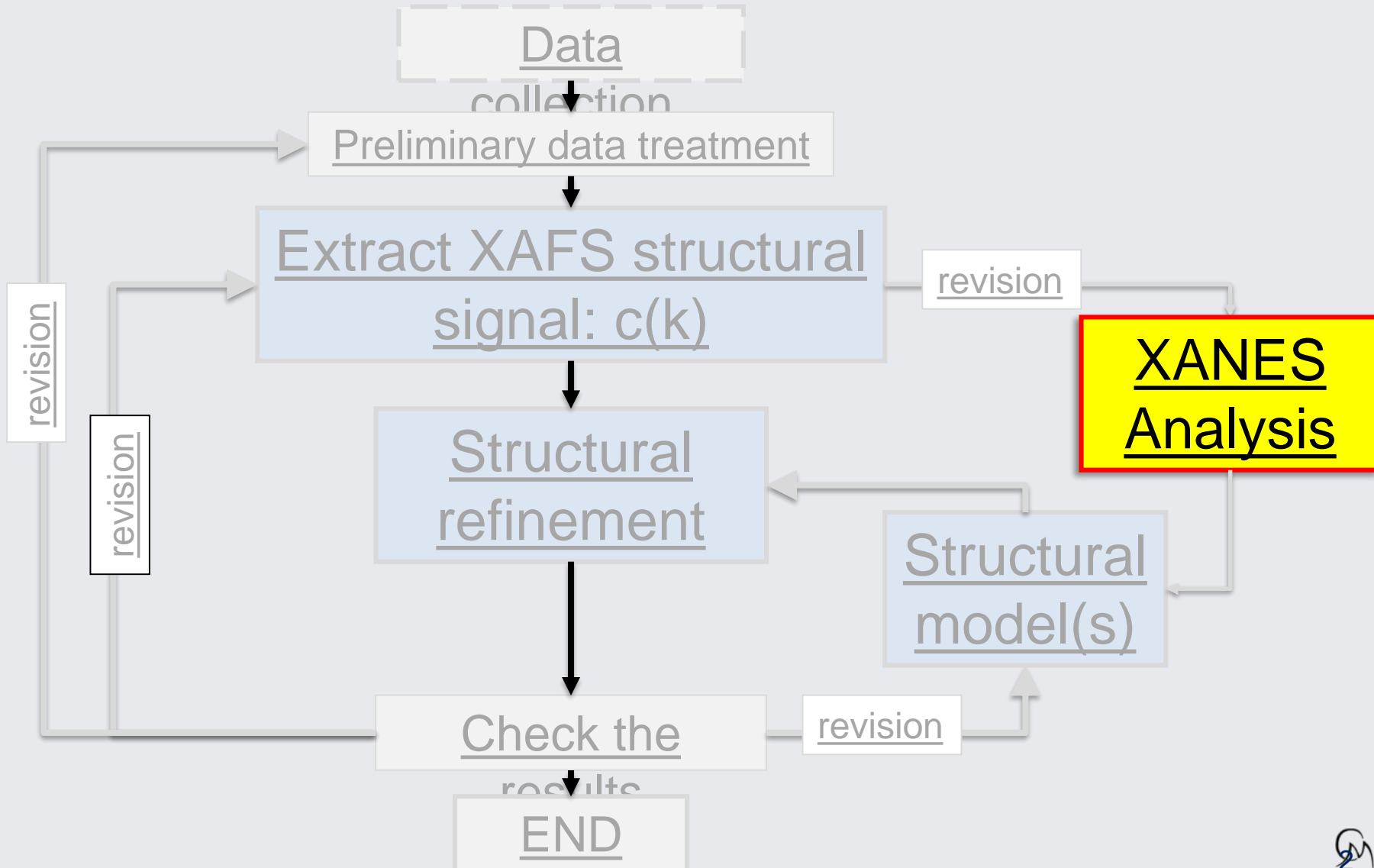
*Dip. Di Scienze, Università Roma Tre, Roma*

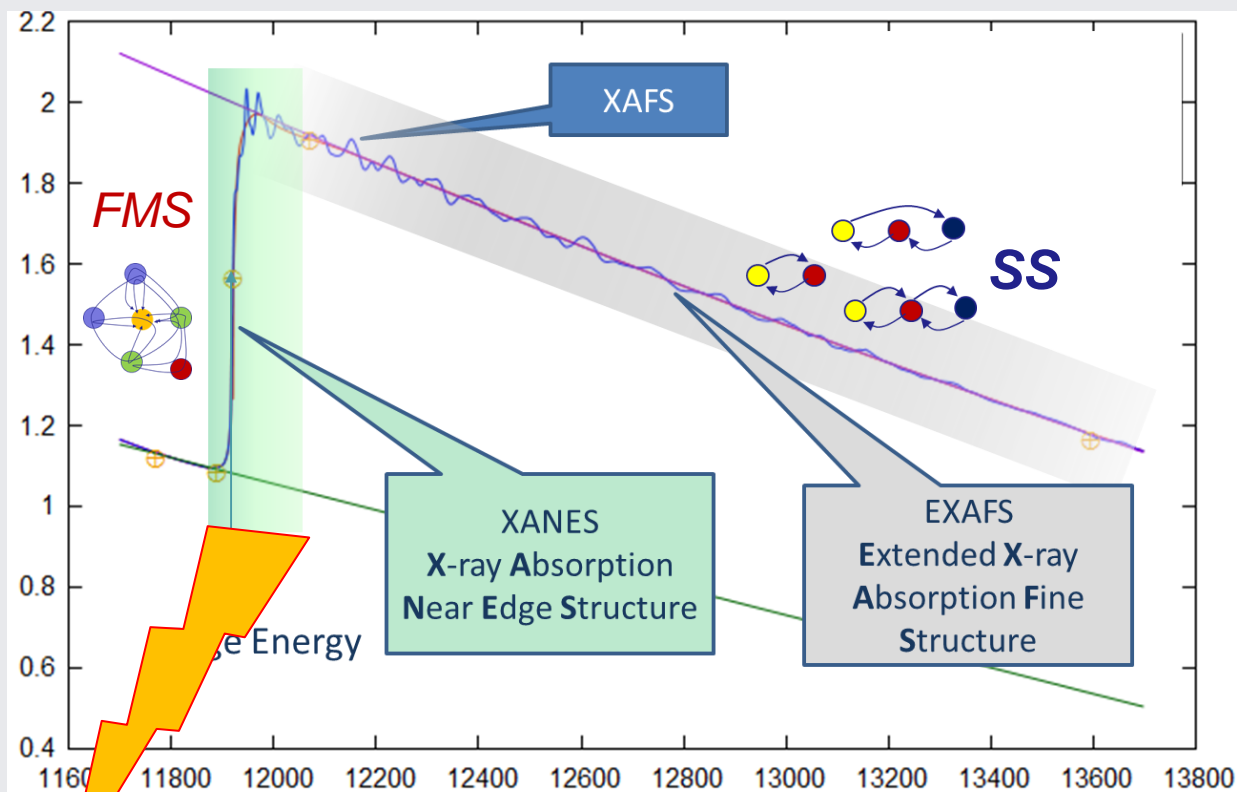
[carlo.meneghini@uniroma3.it](mailto:carlo.meneghini@uniroma3.it)



1st on-line School on Synchrotron Radiation "Gilberto Vlaic":  
Fundamentals, Methods and Application

# *XAFS data ANALYSIS:* *from the experimental data to structural details*





### XANES region:

- **Hard theory**
- **lack of an analytical expression**
- **long computation time**



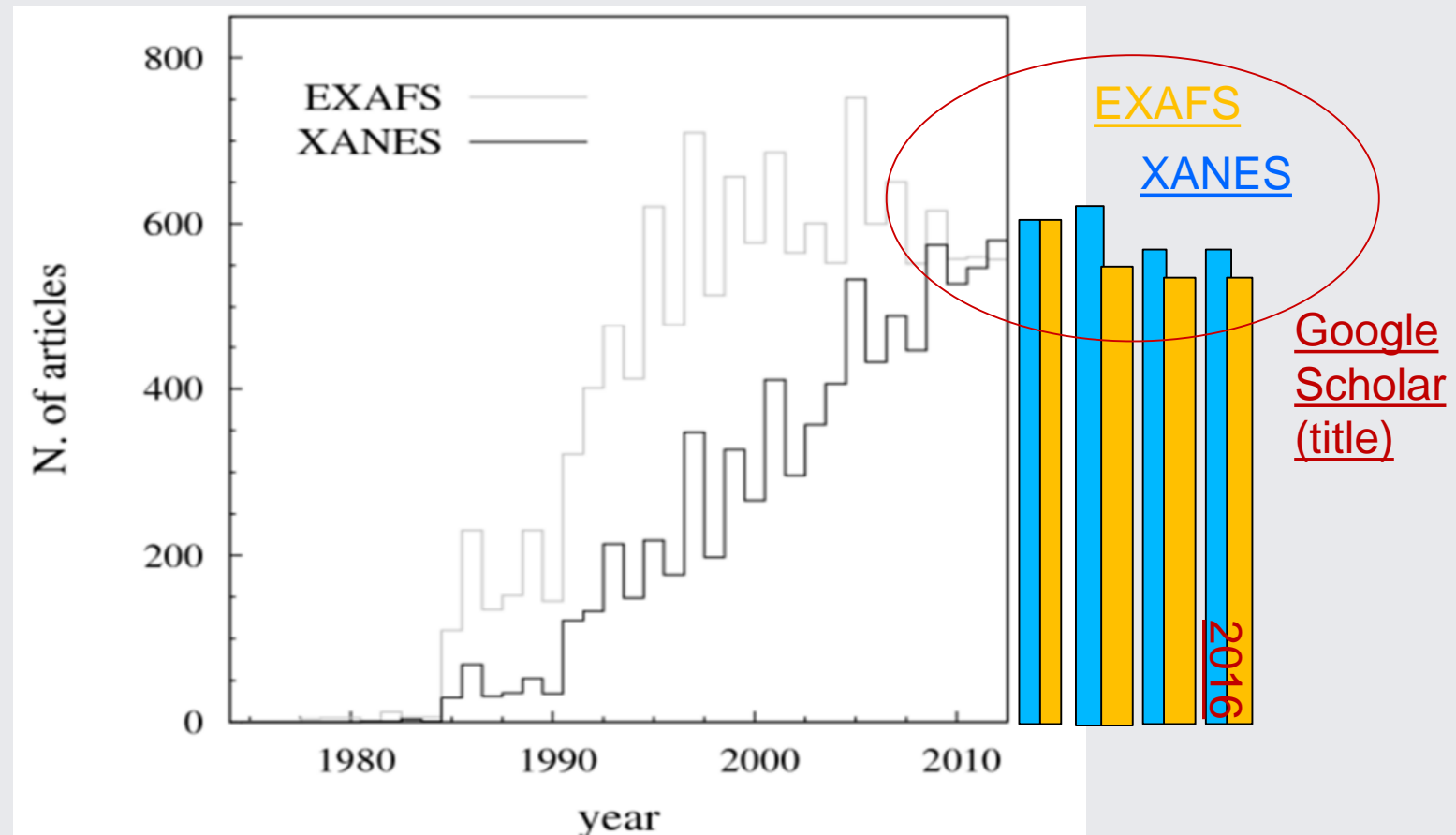
EXAFS region: simple analytical formula suited for data fitting and *easy* structural refinement

$$\chi(k) = \frac{1}{k} \sum A_j \sin(2k\mathbf{r}_j + \psi_j)$$

$$A_j = S_o^2 \frac{N_j}{r_j} |f_j| e^{-2k^2 \sigma_j^2} e_j^{-\frac{2r_j}{\lambda}}$$



# 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 signal is dense of electronic, structural and magnetic and information

## 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).

## 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.

## 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

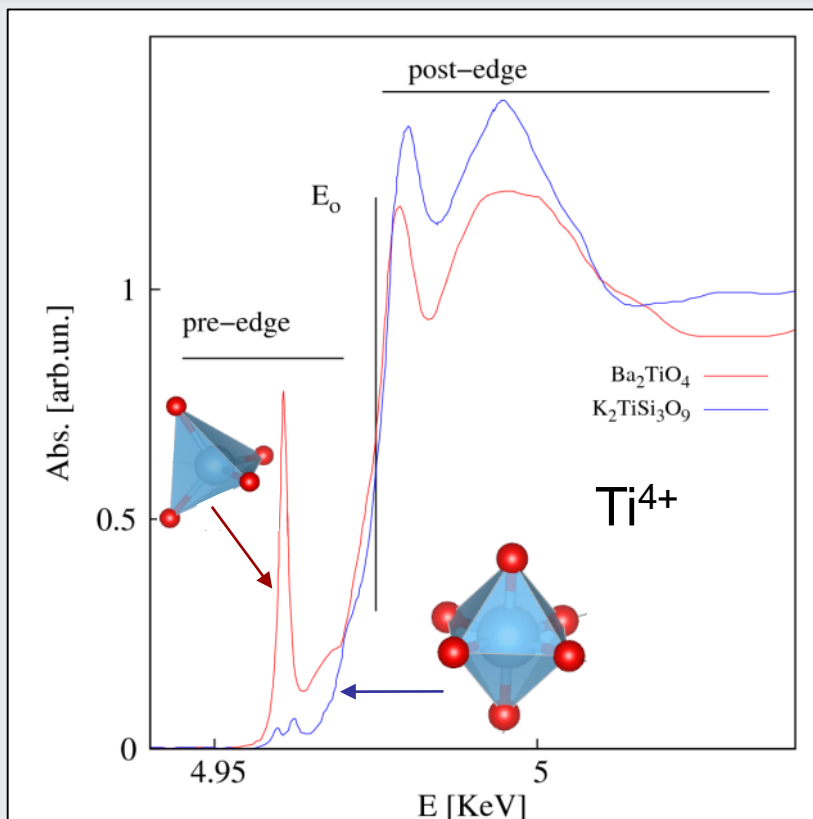
- X ray Magnetic Circular Dichroism (XMCD) signal is an element specific probe for magnetism
- Sum rules at  $L_{2,3}$  edges allow distinguishing orbital and spin contributions to the magnetic moment of the photoabsorber

XANES theory  
is complex

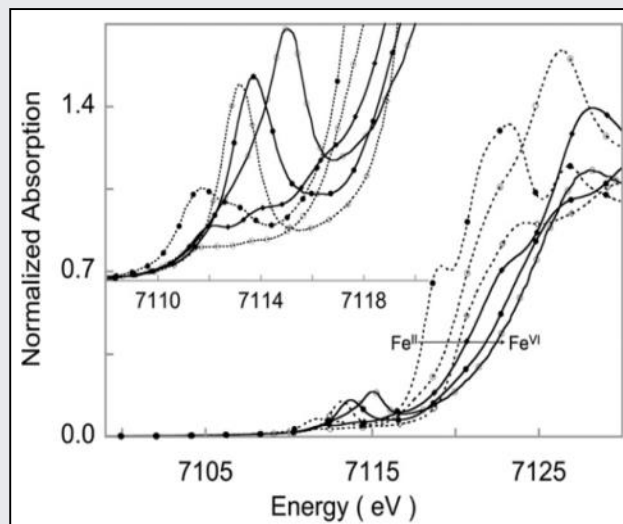


XANES are prone to  
simple interpretation  
for simple and fast  
(semi-)quantitative  
analysis

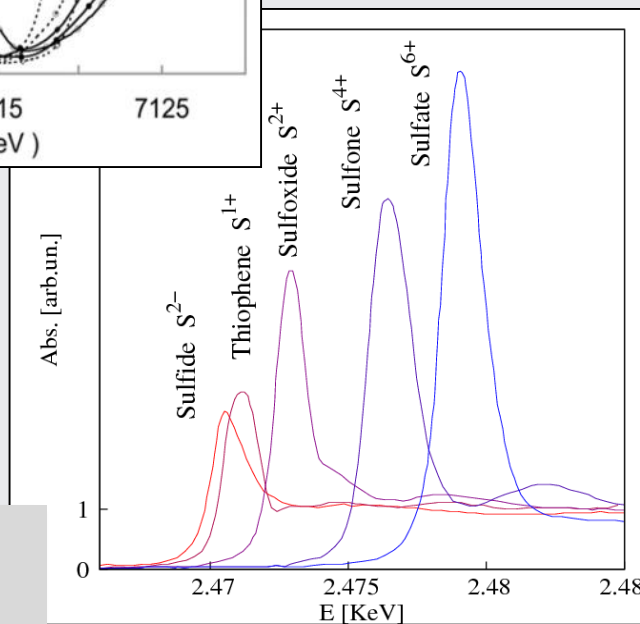
# Deeper insight into the XANES region



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



Fe K edges:  
representative XANES  
Fe in complexes  
R. Sarangi, Coord. Chem.  
Rev. **257** 459–472 (2013)

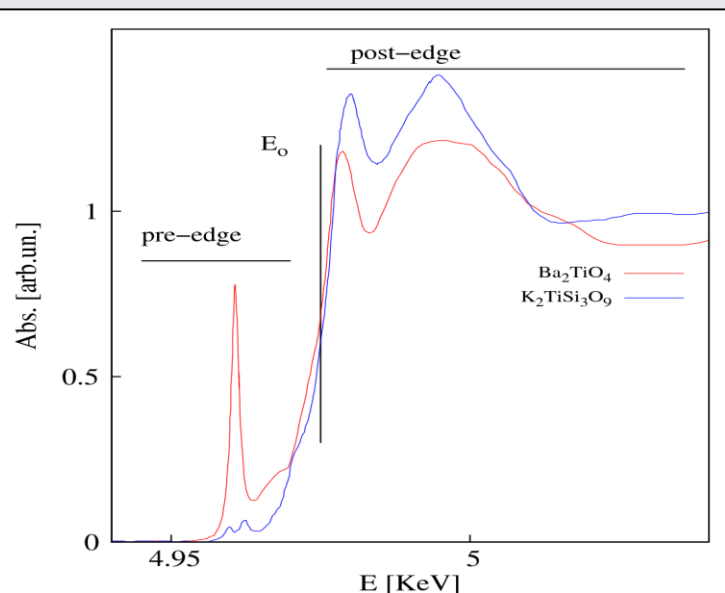


Sulphur K edges:  
chemical shift as a  
function of valence  
state of S-ions

XANES features originate from the **absorber**:

- **electronic nature (valence)**
- **coordination chemistry**
- **coordination geometry:**

# Origin of the XANES features



## Pre-edge

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

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

## Edge ( $E_0$ )

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

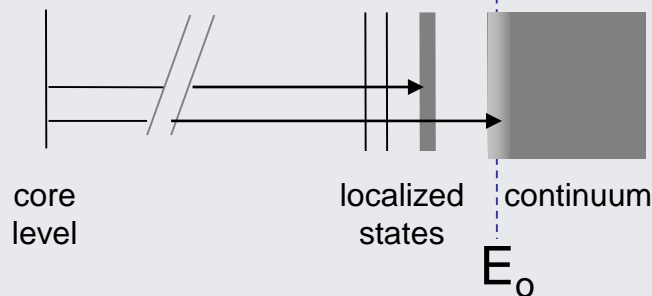
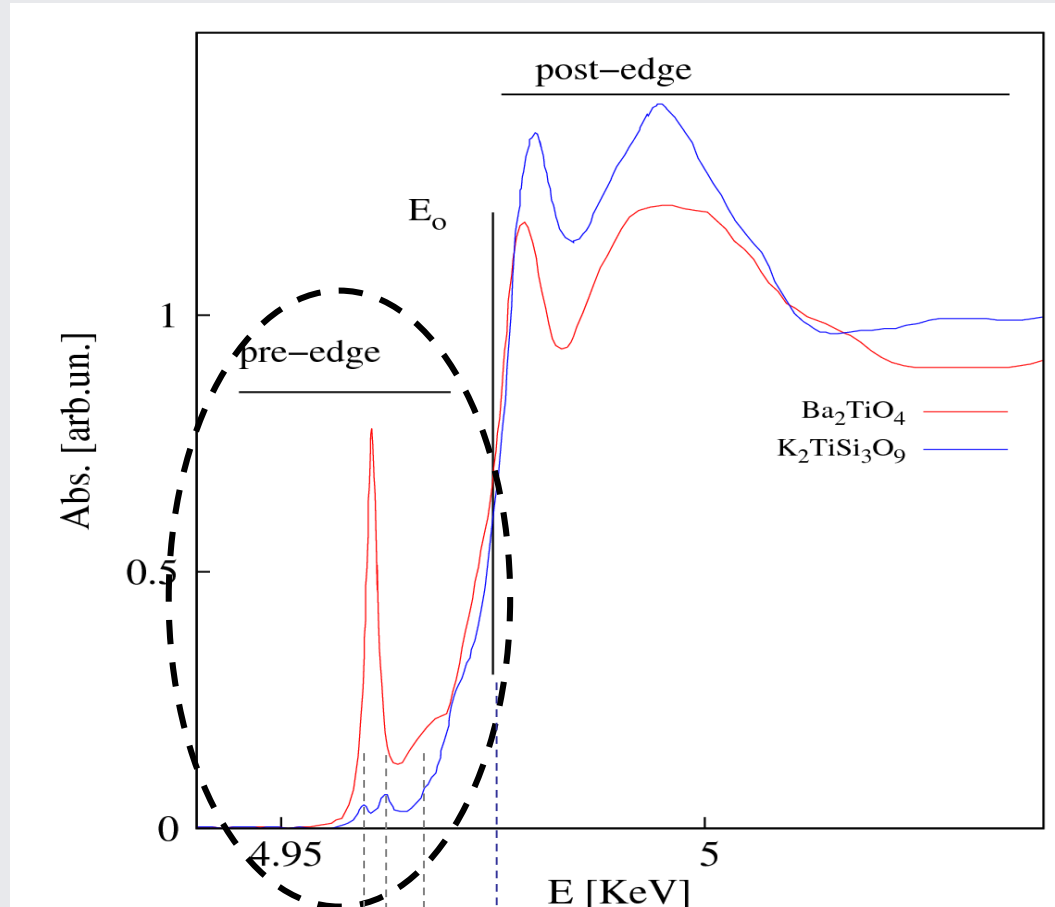
$E_0$  is a function of the absorber oxidation state & binding geometry. It may also increase by several eV per oxidation unit

## Post-edge (XANES)

multiple scattering features (FMS)

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

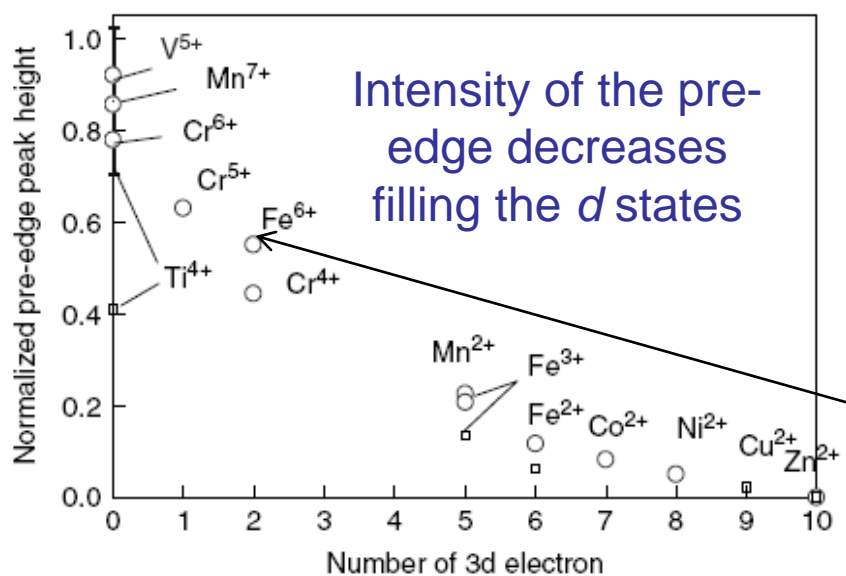
# The Pre-edge region



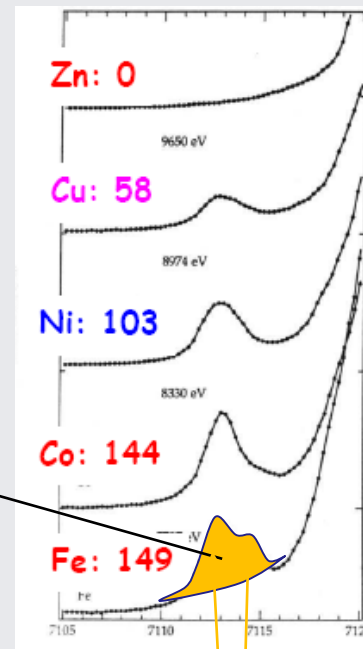
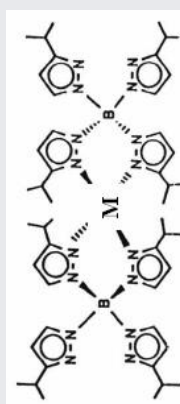
caused by electronic transitions (mainly dipole) to empty bound states near the Fermi level.



# K pre-edges 3d metal oxides: intensity & empty electronic states



Example:  
Pseudo Tetrahedral Metal Complexes  $M(B(3\text{-isopropyl-pyrazol-1-yl})_4)_2$



Pre-edge features are caused by electronic transitions (mainly dipole) to empty states close to the Fermi level.

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

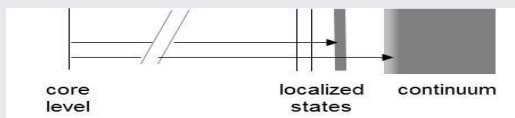
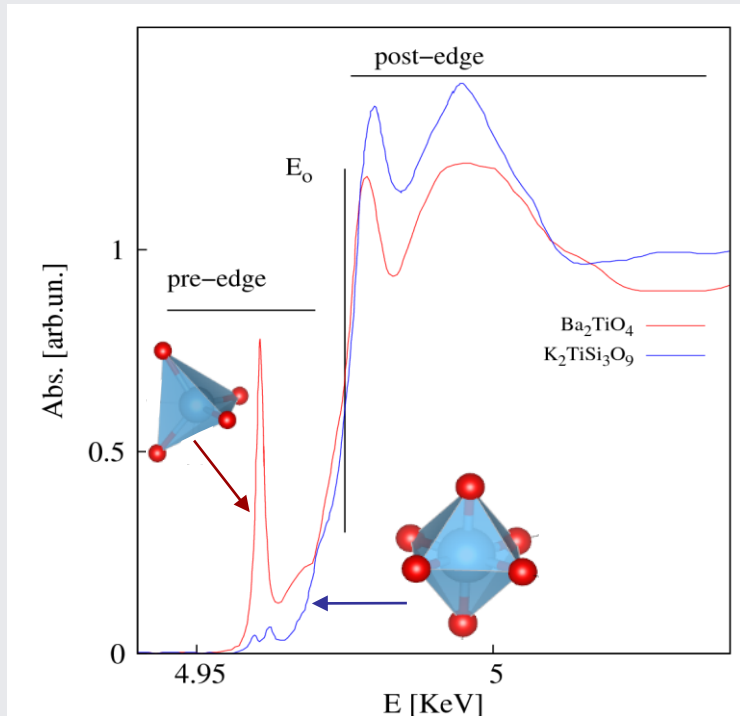
The XANES of the same ions, even in the same oxidation state, may behave differently in different compounds

... depending on **oxidation state** and **coordination geometry** of the absorber

Quantitative Models: multiplet theory

Semi-quantitative approaches:

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

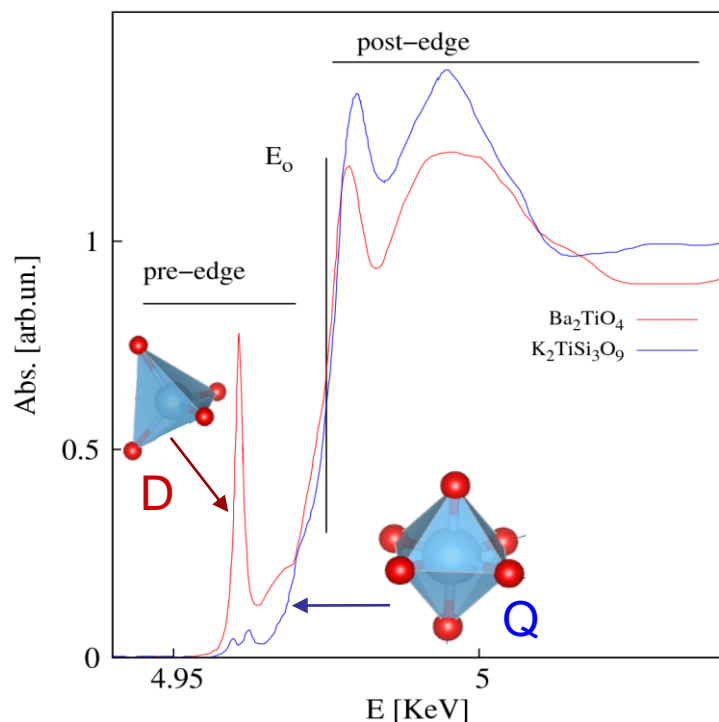
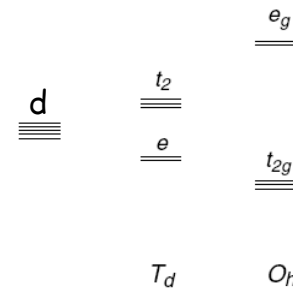


# K edge: mainly $s \rightarrow p$ transitions

$$I_{sd} (\text{quadrupole}) \sim 10^{-2} I_{sp} (\text{dipole})$$

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

crystalline field splitting of  $d$  atomic orbitals



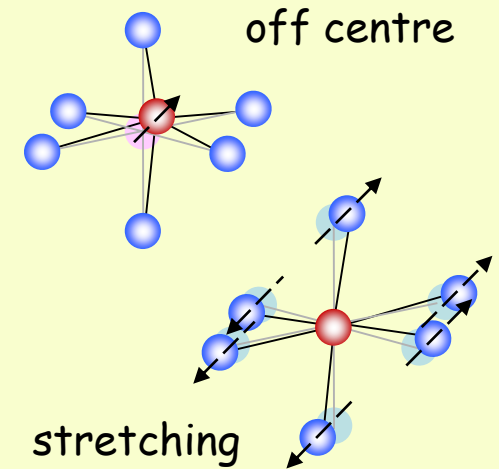
**Table 1.** Lists of irreducible representations and the relating functions in  $T_d$ ,  $O_h$ , and  $D_{4h}$  point groups

$T_d$	
p	d
$A_1$	$x^2 + y^2 + z^2$
$A_2$	$(2z^2 - x^2 - y^2, x^2 - y^2)$
$E$	$(R_x, R_y, R_z)$
$T_1$	$(x, y, z)$
$T_2$	$(xz, yz, xy)$
$O_h$	
p	d
$A_{1g}$	$x^2 + y^2 + z^2$
$A_{2g}$	$(2z^2 - x^2 - y^2, x^2 - y^2)$
$E_g$	$(R_x, R_y, R_z)$
$T_{1g}$	$(x, y, z)$
$T_{2g}$	$(xz, yz, xy)$
$A_{1u}$	
$A_{2u}$	
$E_u$	
$T_{1u}$	
$T_{2u}$	

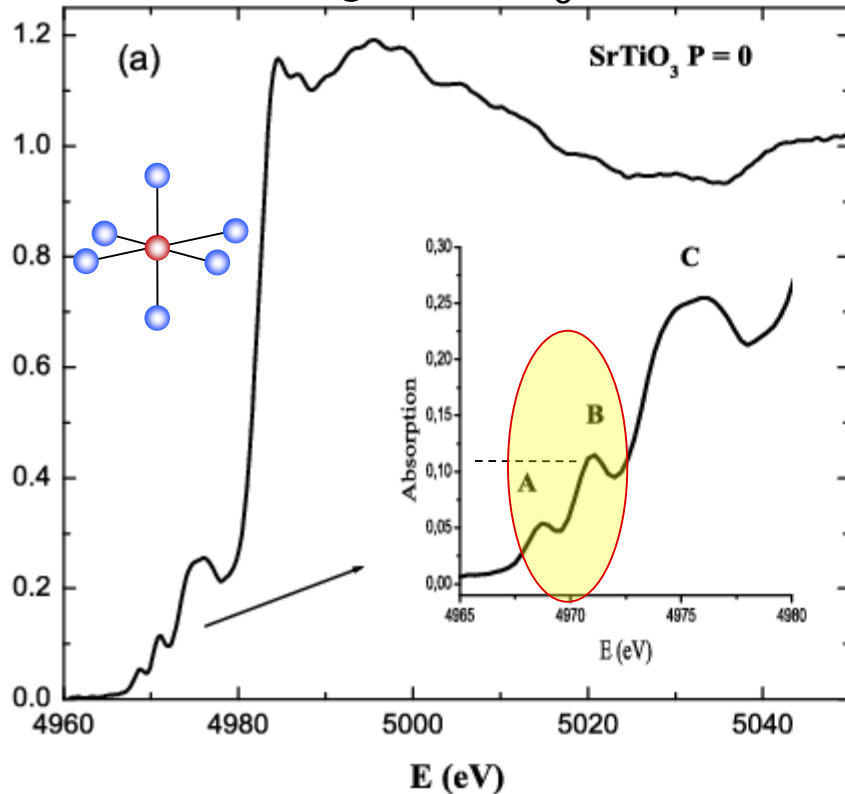
Yamamoto *X-Ray Spectrom.* 2008; **37**: 572–584

# p-d mixing and sensitivity to local symmetry of $\text{TiO}_6$ units

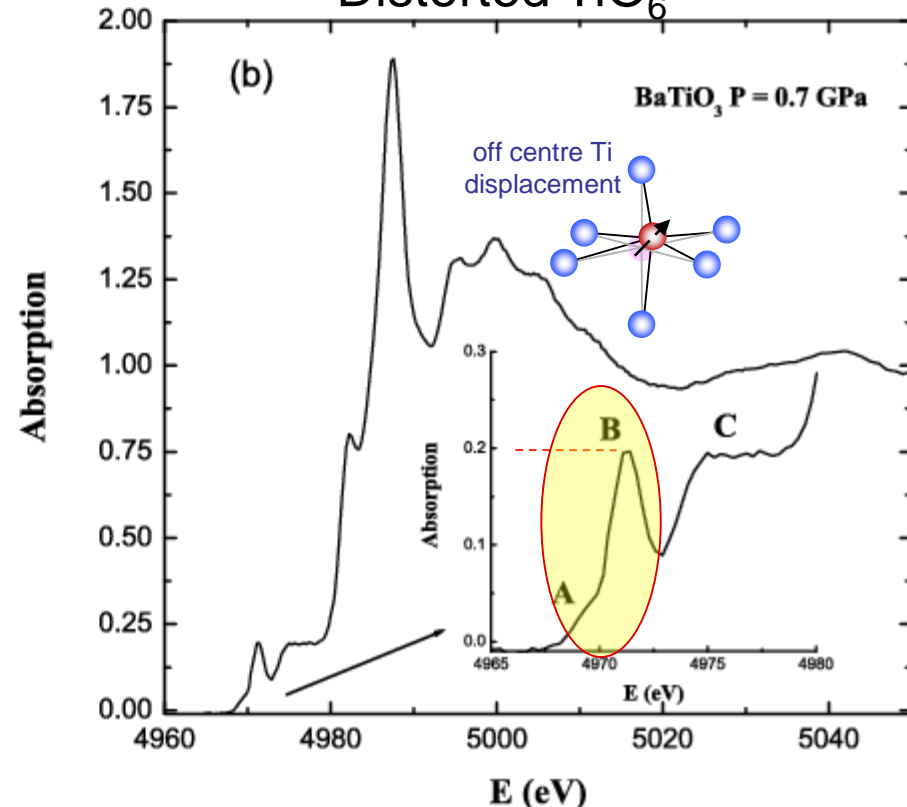
Off centre displacement and stretching of the octahedron decreases the local symmetry (non-centro-symmetric) allowing some degree of *p-d* mixing, this affect the pre-edge peaks intensity



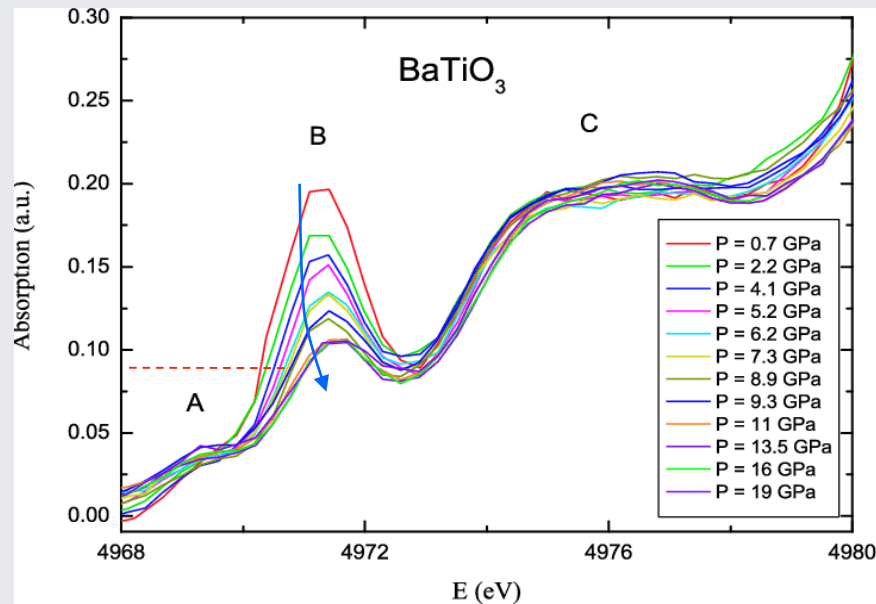
Regular  $\text{TiO}_6$



Distorted  $\text{TiO}_6$



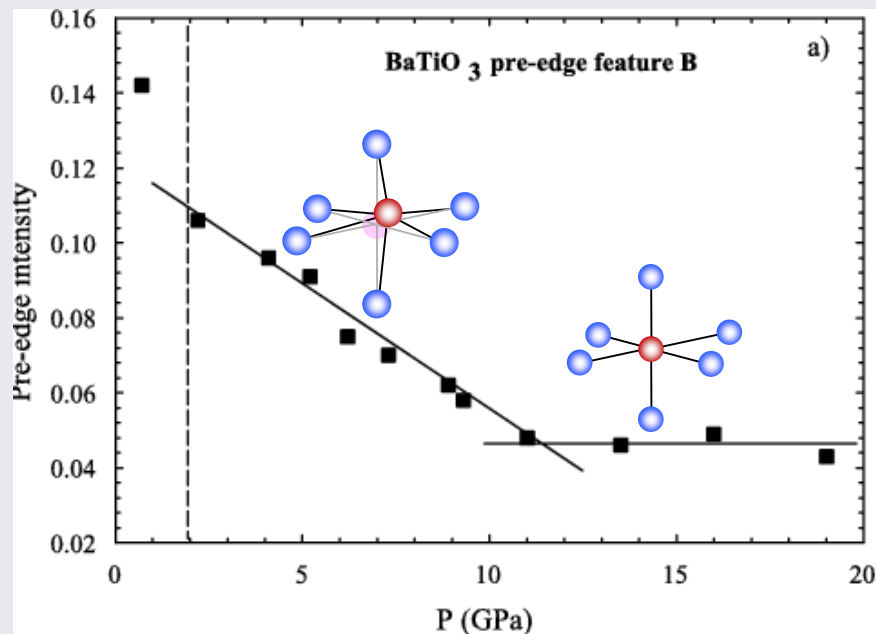
# Example: hydrostatic pressure reduces $\text{TiO}_6$ distortions in $\text{BaTiO}_3$ and suppress ferroelectricity



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,

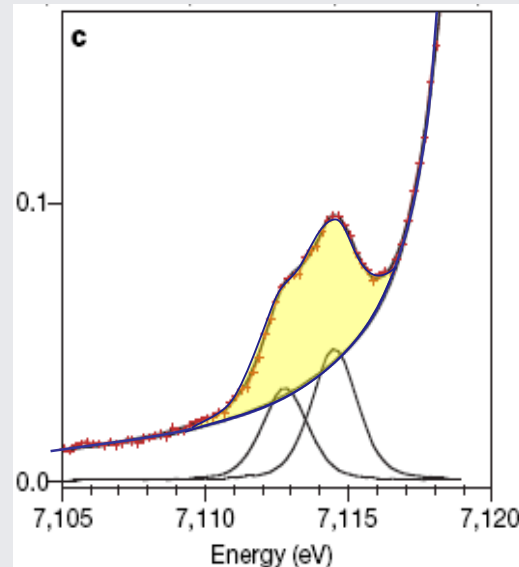
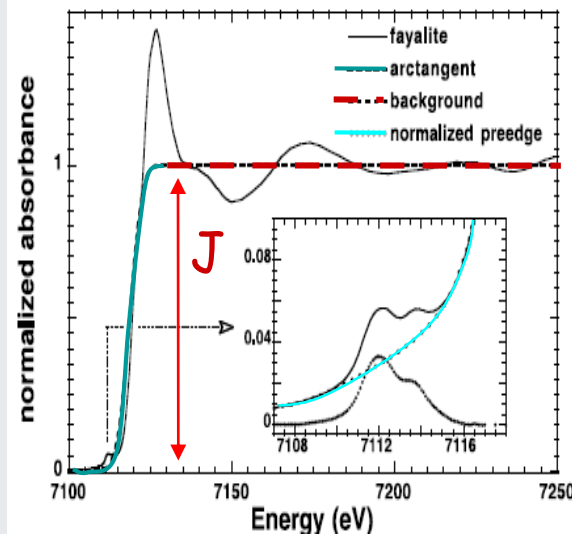
the hybridization of the Ti  $3d$  electronic states with the  $2p$  electronic states of the surrounding oxygen is at the minimum



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

# Selection of normalized pre-edge features

data normalization and background

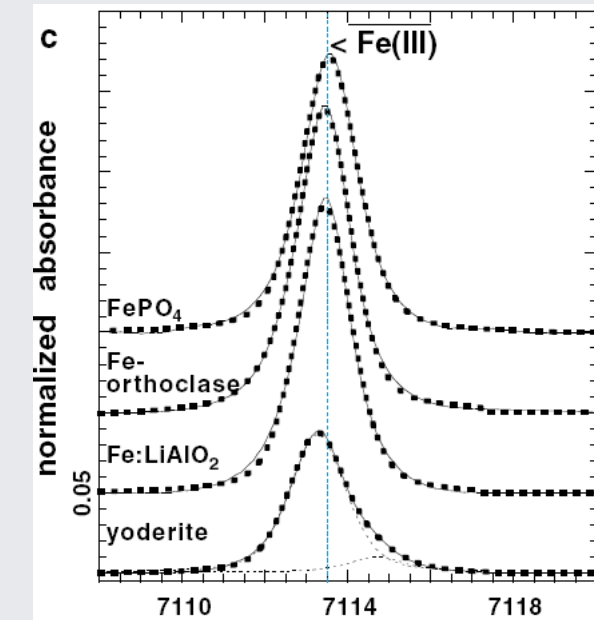
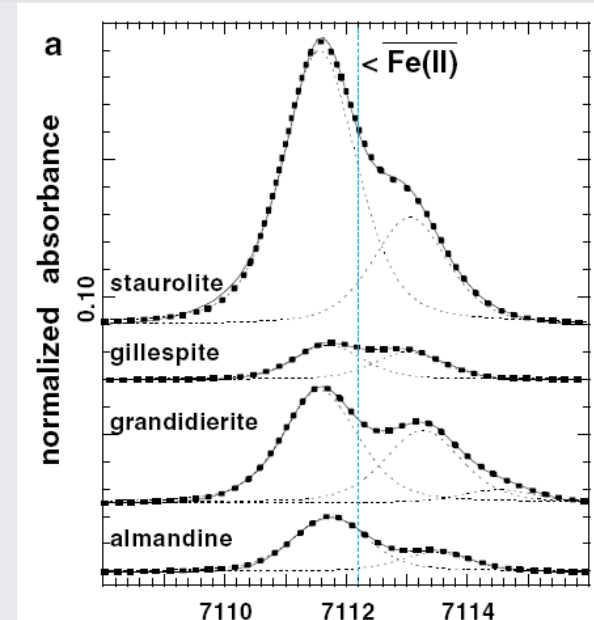


normalization: Jump = 1

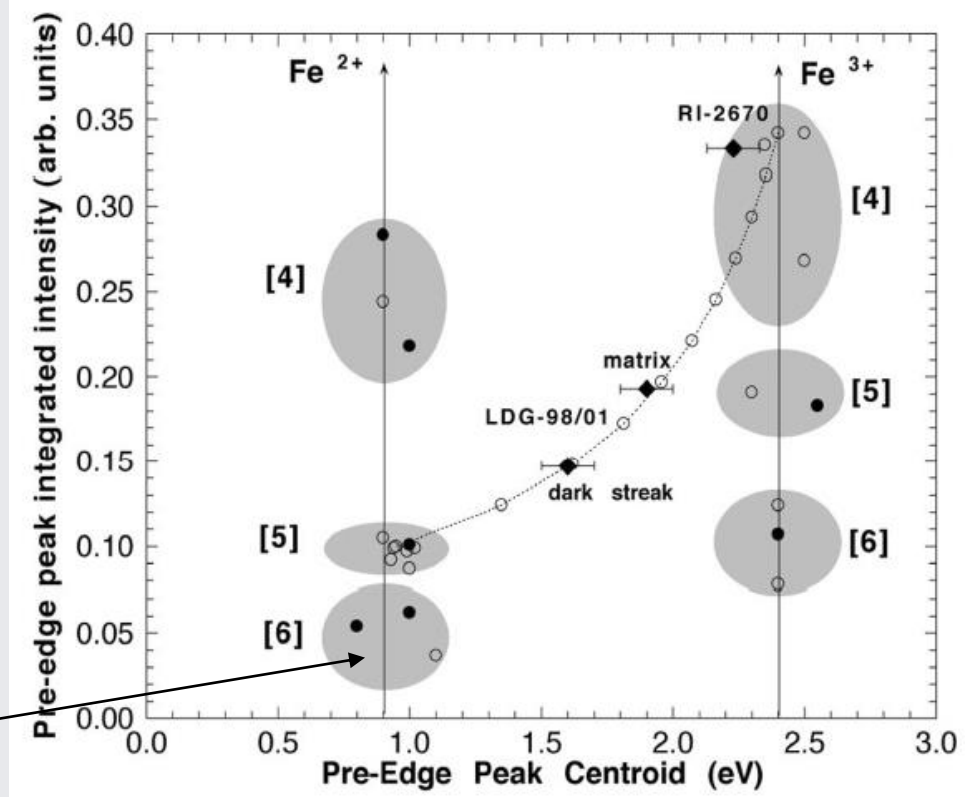
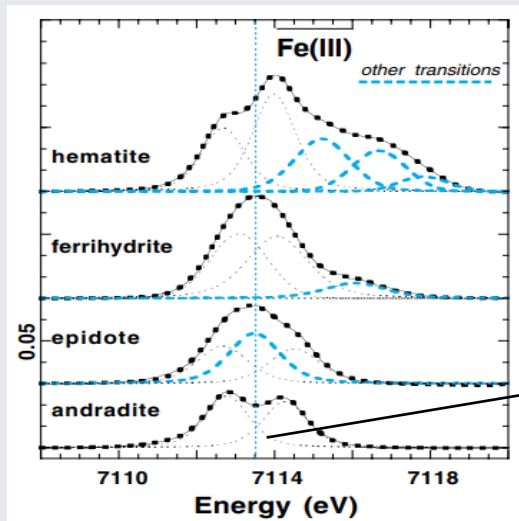
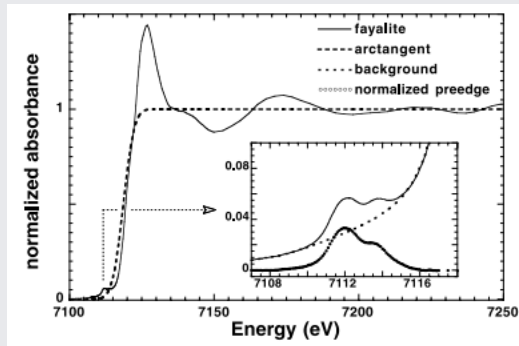
arctangent: transitions to continuum states,

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)



# The Iron case: the average valence and coordination chemistry from the pre-edge peak shape/position



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

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

MAX WILKE,<sup>1,\*</sup> FRANÇOIS FARGES,<sup>1,2</sup> PIERRE-EMMANUEL PETIT,<sup>3</sup> GORDON E. BROWN JR.,<sup>2,4</sup> AND FRANÇOIS MARTIN<sup>5</sup>

850 cit. (sept.2019, Scholar Google)

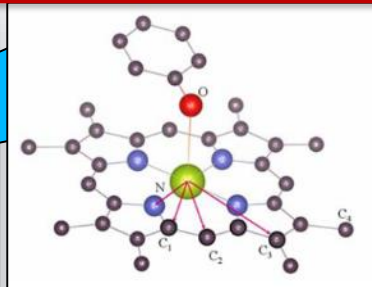
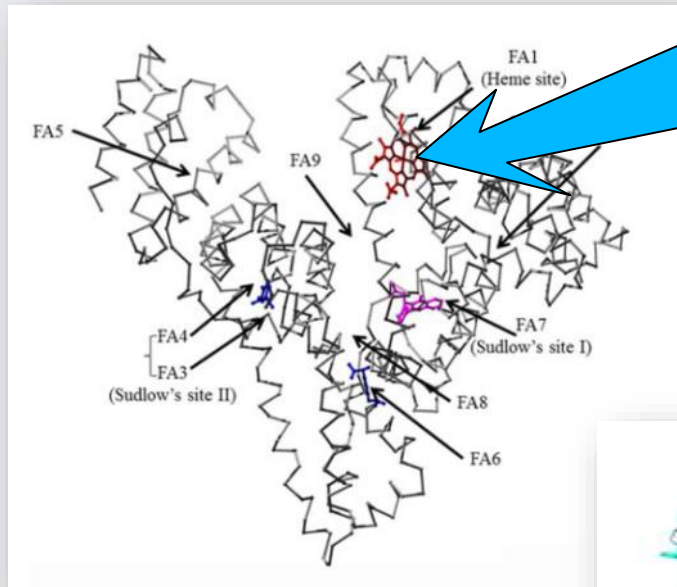
It is possible to understand the Fe coordination number looking at the intensity/area of the pre-edge peaks in comparison with reference compounds data



# The case of Fe in metallo-proteins:

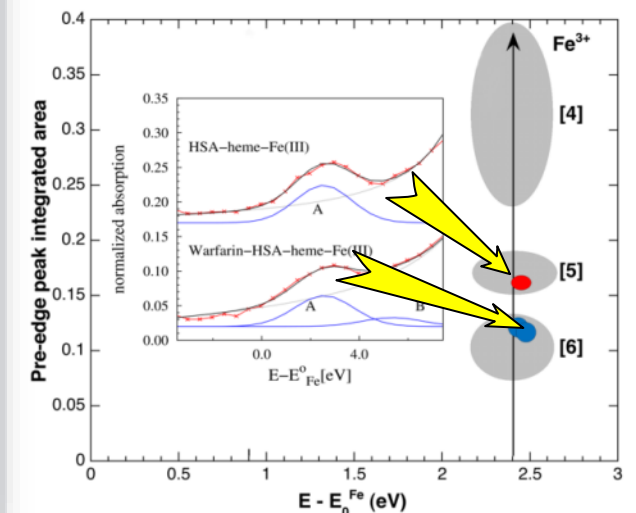
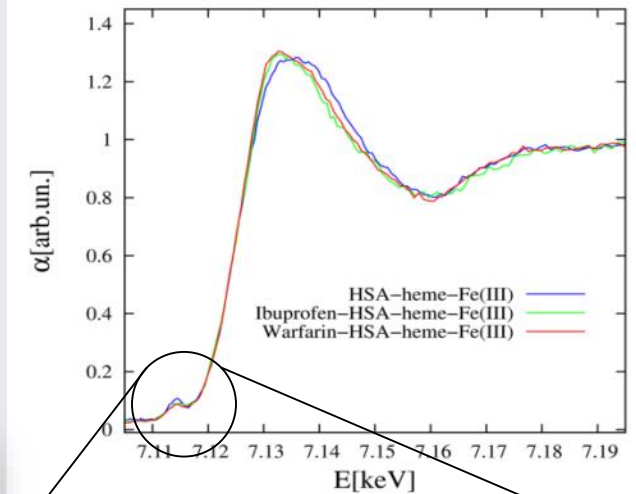
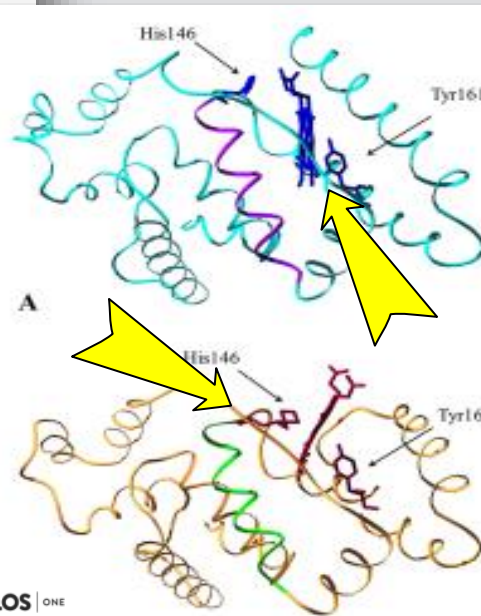
Biophysics

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



Heme (Fe) site

Human Serum Albumin



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<sup>1\*</sup>, Loris Leboffe<sup>1,2\*</sup>, Monica Bionducci<sup>1</sup>, Gabriella Fanali<sup>3</sup>, Massimiliano Meli<sup>4</sup>, Giorgio Colombo<sup>4</sup>, Mauro Fasano<sup>3</sup>, Paolo Ascenzi<sup>2,5\*</sup>, Settimio Mobilio<sup>1</sup>



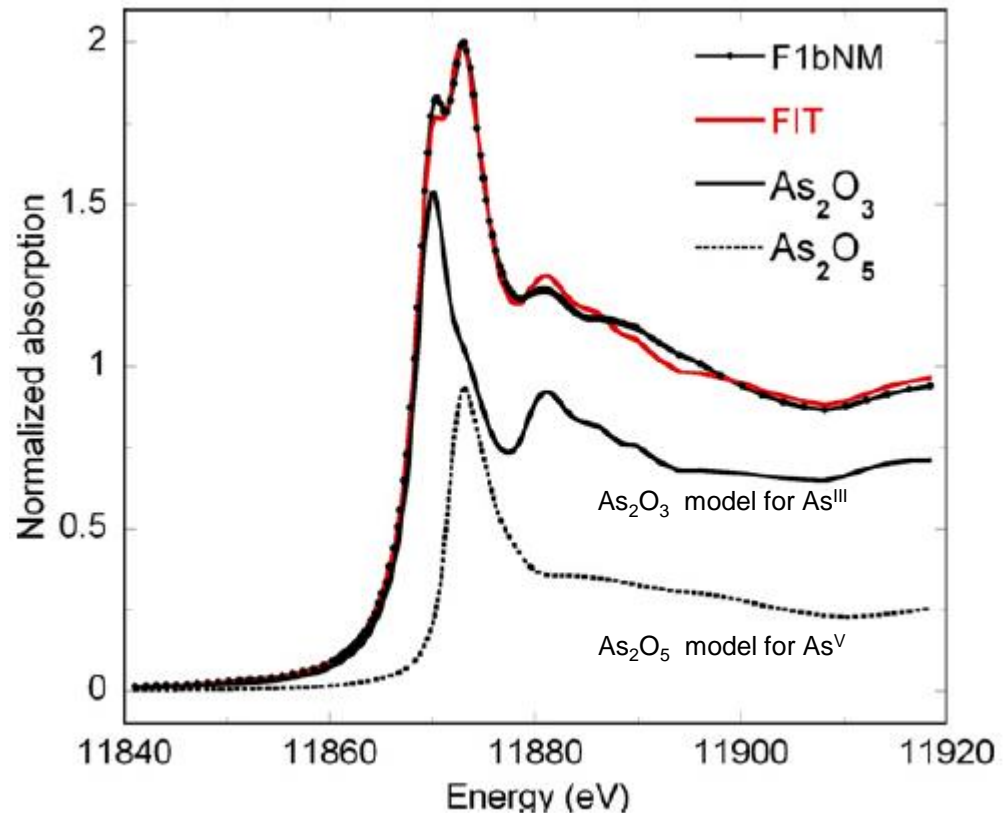
## 2. Analysis of mixtures: *Linear Combination Analysis*

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

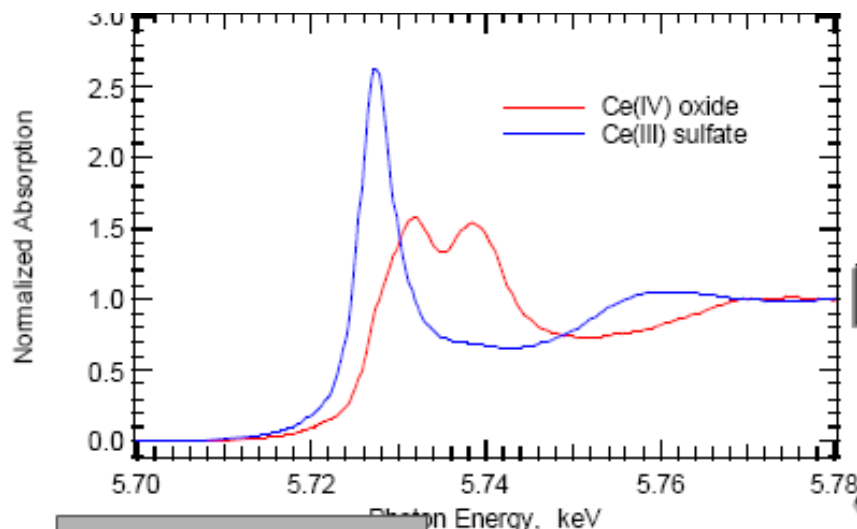
$$R^2 = \sum_i (\mu^{exp}(E_i) - \mu^{th}(E_i))^2$$

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

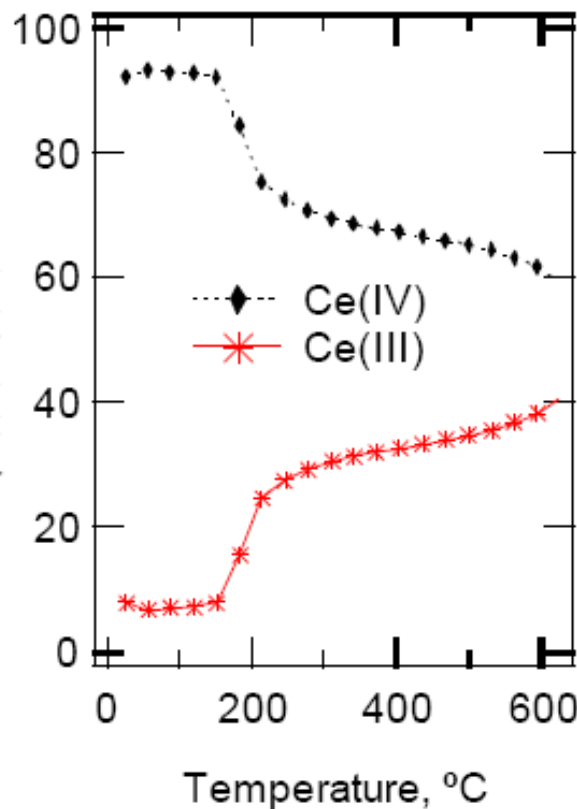
As adsorption in Natural Calcite samples



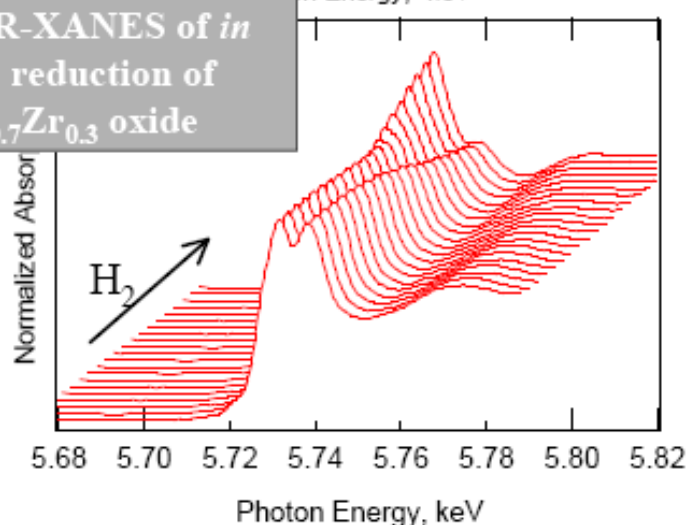
# XANES - LCA for Catalysis



Fit experimental data to linear combination of known reference compounds

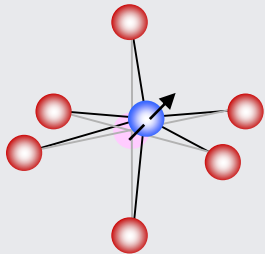
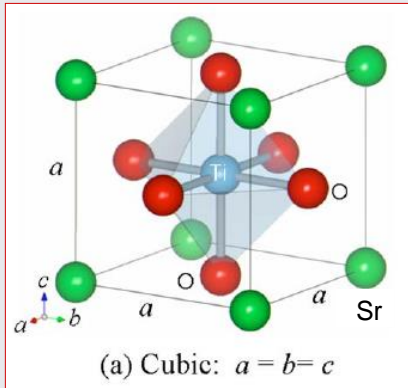
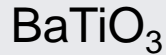


TPR-XANES of *in situ* reduction of  $\text{Ce}_{0.7}\text{Zr}_{0.3}$  oxide



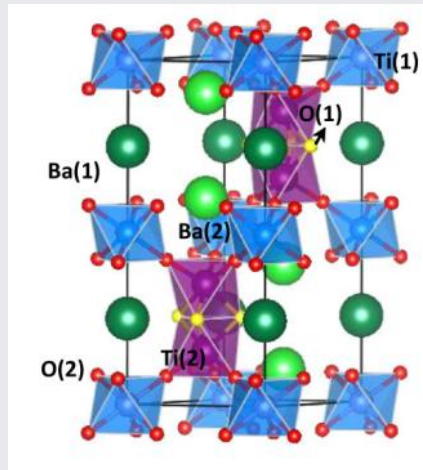
LC-XANES fit to determine amount of Ce(III) and Ce(IV) present as function of temperature

# Advanced materials: looking for magneto-electric coupling

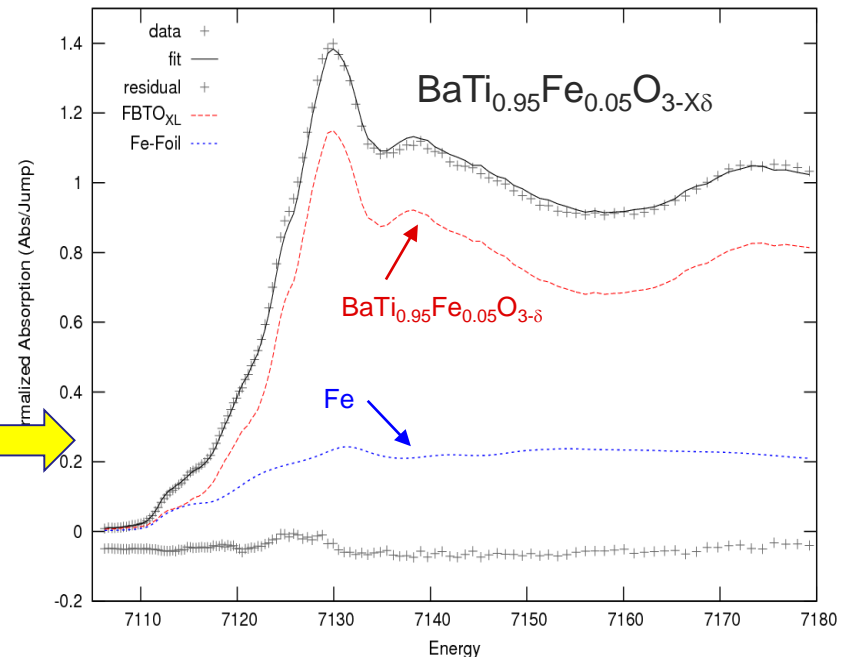


$\text{BaTiO}_3$  is **ferroelectric**: off center displacement of  $\text{Ti}^{4+}$  ions produces a permanent electric dipole in  $\text{TiO}_6$  molecules

**Note:** XRD can't show Fe crystalline phase because 1% of  $\text{Fe}^0$



doping with magnetic ions (Fe) may provide some **magnetoelectric coupling** and **stabilize the ferroelectric phase**



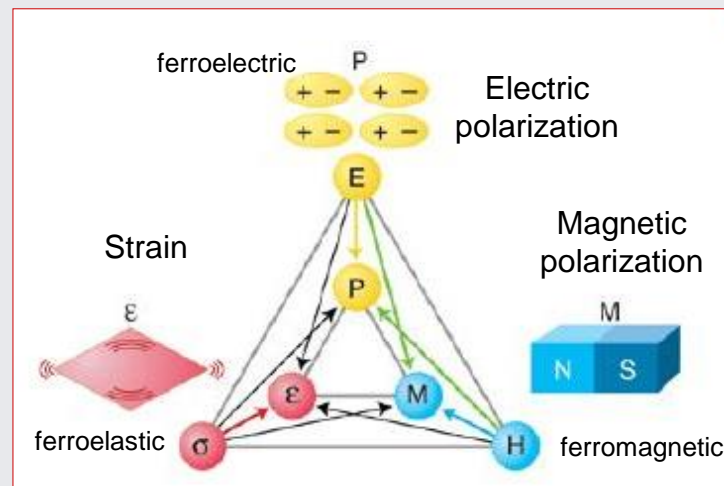
Large Oxygen vacancies causes the Fe ions segregating as metallic  $\text{Fe}^0$  phase, the sample is no more homogeneous at the short range scale, **wrong magneto-electric understanding**

# 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



# Analysis of mixtures: Linear Combination Analysis

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

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

