



ALBA SYNCHROTRON:  
NEW TOOLS FOR MATERIALS CHARACTERIZATION  
ALBA November 13-14<sup>th</sup> 2014

# X-Ray Absorption Spectroscopy at CLÆSS

**Marta Ávila**

*CLÆSS - Core Level Absorption and Emission Spectroscopies*

# Outline

1. What is x-ray absorption spectroscopy (XAS)?
2. What can be used for?
3. Applications

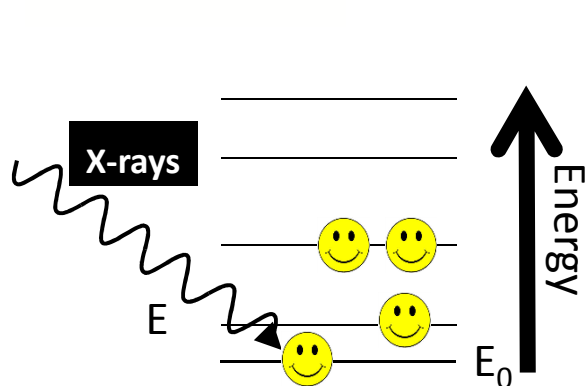
# 1. What is X-ray absorption spectroscopy?



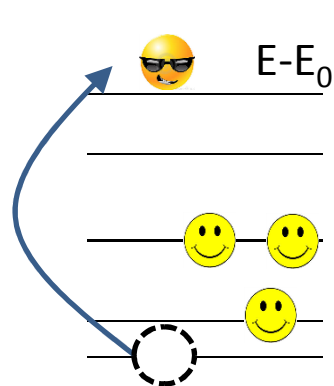
Peter BEHRENS

Trends Anal.Chem., v.11, n.7, p.237-244, 1992.

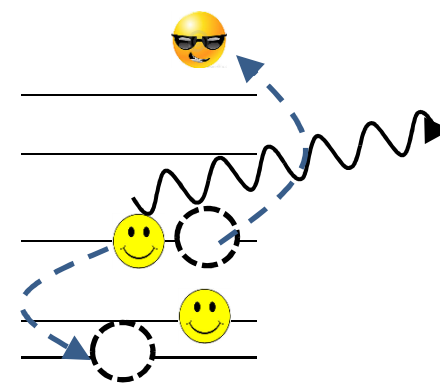
# 1. What is X-ray absorption spectroscopy?



An incident x-ray of energy  $E$  is absorbed, exciting a core electron of binding energy  $E_0$



emitting a photo-electron with kinetic energy  $(E-E_0)$ , to some unoccupied state

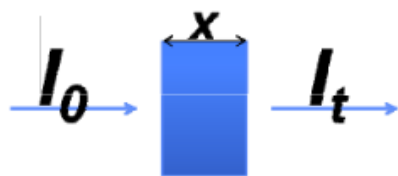


The core state is filled (1 or 2 fs later), ejecting a fluorescent x-ray or an Auger electron



## Absorption

Lambert-Beer:  $I_t = I_0 e^{-\mu x}$   
 $\mu x = -\ln(I/I_0)$   
 $\mu$  = x-ray absorption coefficient  
 $x$  = thickness of the sample



## Fluorescence

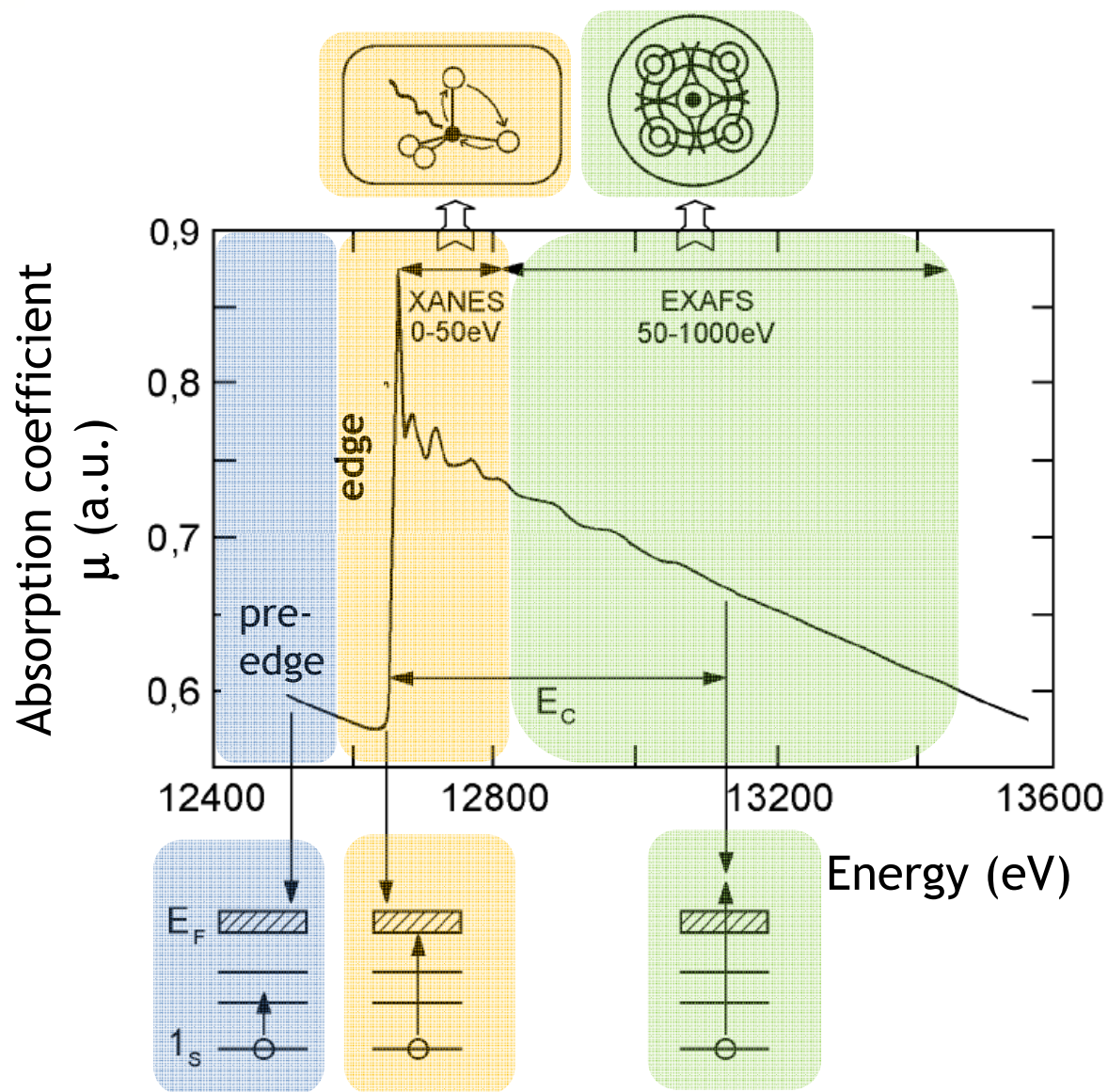
Auger electrons

Proportional to absorption

- 
- hydrogen 1  
H  
1.0079
- lithium 3  
Li  
6.941
- beryllium 4  
Be  
9.0122
- sodium 11  
Na  
22.9898
- magnesium 12  
Mg  
24.3047
- boron 5  
B  
10.811
- carbon 6  
C  
12.011
- nitrogen 7  
N  
14.007
- oxygen 8  
O  
15.999
- fluorine 9  
F  
18.998
- neon 10  
Ne  
20.180
- aluminum 13  
Al  
26.982
- silicon 14  
Si  
28.086
- phosphorus 15  
P  
30.974
- sulfur 16  
S  
32.06
- chlorine 17  
Cl  
35.45
- argon 18  
Ar  
39.948
- potassium 19  
K  
39.098
- calcium 20  
Ca  
40.078
- scandium 21  
Sc  
44.956
- titanium 22  
Ti  
47.867
- vanadium 23  
V  
50.942
- chromium 24  
Cr  
51.996
- manganese 25  
Mn  
54.938
- iron 26  
Fe  
55.845
- cobalt 27  
Co  
58.933
- nickel 28  
Ni  
58.693
- copper 29  
Cu  
63.546
- zinc 30  
Zn  
65.38
- gallium 31  
Ga  
69.723
- germanium 32  
Ge  
72.631
- arsenic 33  
As  
74.922
- selenium 34  
Se  
78.96
- bromine 35  
Br  
79.904
- krypton 36  
Kr  
83.80
- rubidium 37  
Rb  
85.468
- strontium 38  
Sr  
87.62
- yttrium 39  
Y  
88.906
- zirconium 40  
Zr  
91.224
- niobium 41  
Nb  
92.906
- molybdenum 42  
Mo  
95.94
- technetium 43  
Tc  
98.906
- ruthenium 44  
Ru  
101.07
- rhodium 45  
Rh  
102.91
- silver 46  
Ag  
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- cadmium 47  
Cd  
112.41
- indium 48  
In  
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- tin 49  
Sn  
118.71
- antimony 50  
Sb  
121.76
- tellurium 51  
Te  
127.6
- iodine 52  
I  
126.91
- xenon 54  
Xe  
131.29
- cesium 55  
Cs  
132.91
- barium 56  
Ba  
137.33
- lanthanum 57  
La  
138.91
- cerium 58  
Ce  
140.12
- praseodymium 59  
Pr  
140.91
- neodymium 60  
Nd  
144.24
- promethium 61  
Pm  
144.91
- samarium 62  
Sm  
150.36
- europium 63  
Eu  
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- gadolinium 64  
Gd  
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- terbium 65  
Tb  
158.93
- dysprosium 66  
Dy  
162.50
- holmium 67  
Ho  
164.93
- erbium 68  
Er  
167.26
- thulium 69  
Tm  
168.93
- ytterbium 70  
Yb  
173.05
- lutetium 71  
Lu  
174.97
- hafnium 72  
Hf  
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- tantalum 73  
Ta  
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- tungsten 74  
W  
183.84
- reuterium 75  
Re  
186.21
- osmium 76  
Os  
190.23
- iridium 77  
Ir  
192.22
- platinum 78  
Pt  
195.08
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Au  
196.97
- mercury 80  
Hg  
200.59
- thallium 81  
Tl  
204.38
- lead 82  
Pb  
207.2
- bismuth 83  
Bi  
208.98
- polonium 84  
Po  
209
- astatine 85  
At  
210
- radon 86  
Rn  
222
- francium 87  
Fr  
223
- radium 88  
Ra  
226
- actinium 89  
Ac  
227
- thorium 90  
Th  
232
- protactinium 91  
Pa  
231
- uranium 92  
U  
238
- neptunium 93  
Np  
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- plutonium 94  
Pu  
244
- americium 95  
Am  
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- curium 96  
Cm  
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Bk  
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- californium 98  
Cf  
251
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Es  
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Fm  
257
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Md  
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At  
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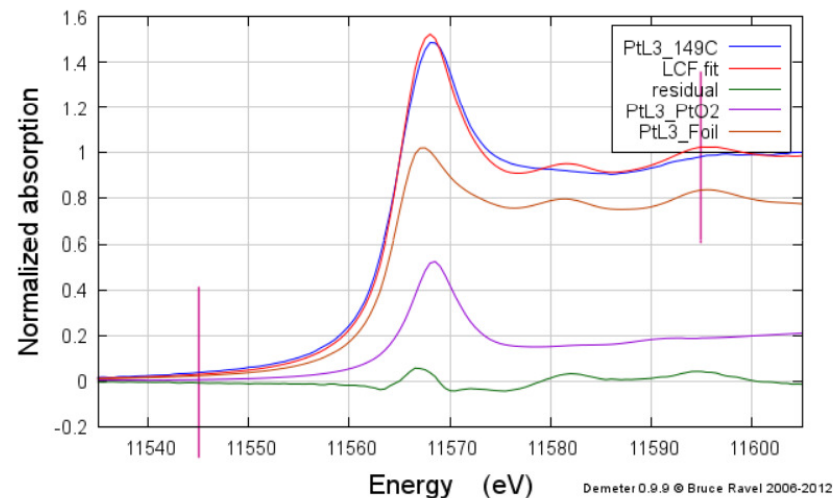
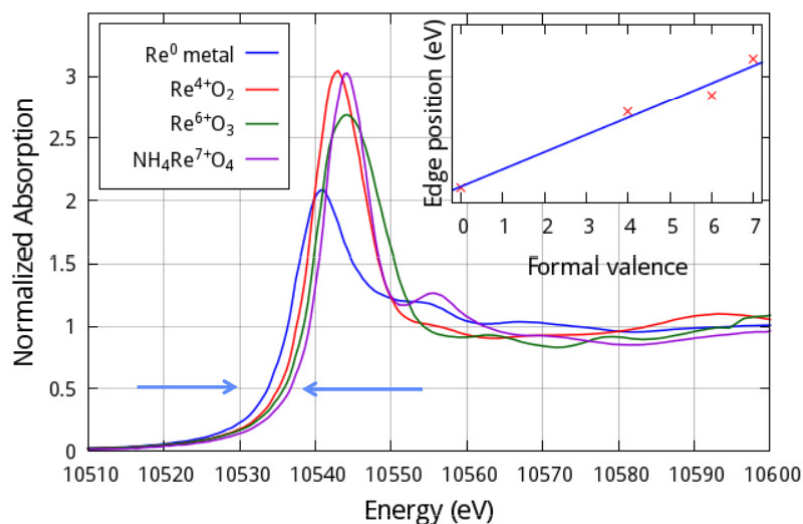
# 1. What is X-ray absorption spectroscopy?



# 1. What is X-ray absorption spectroscopy?

## XANES (X-ray Absorption Near Edge Structure)

- The position of the absorption edge is different for different **oxidation states**. Charged elements require higher energy to remove the electrons causing the edge to shift.
- Linear combination fitting (LCF) using standards to reproduce the measured spectrum to determine the **relative amount of each standard** in the measured spectrum.



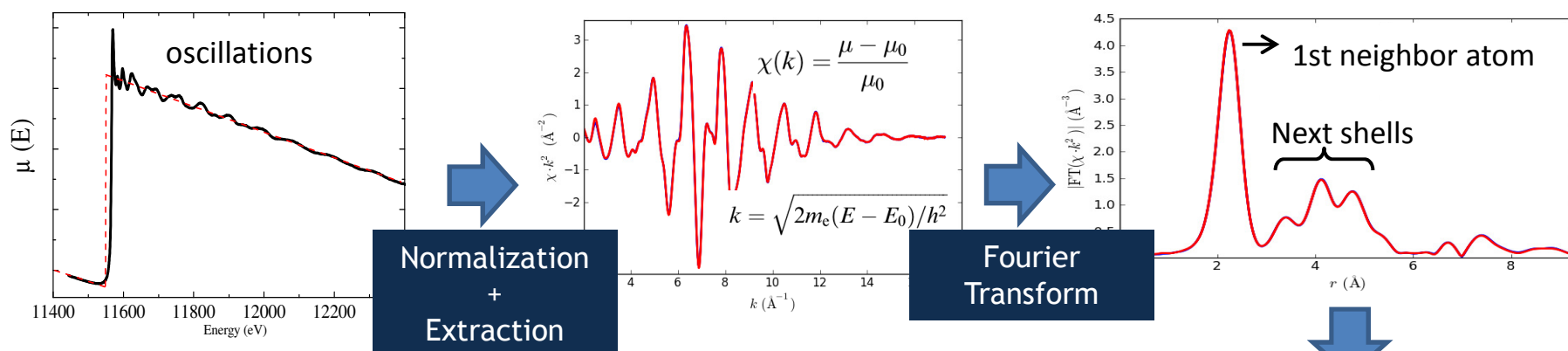
Good knowledge of your sample, **standards should be a good representation** of Pt species in the sample.



# 1. What is X-ray absorption spectroscopy?

## EXAFS (Extended X-ray Absorption Fine Structure)

- The data treatment is a “little bit” more complex than in XANES.



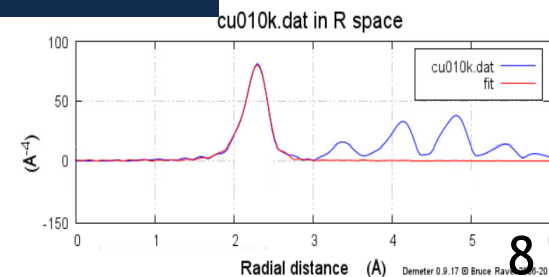
- More information can be extracted

**Bond distances**

**Coordination number**

**Static and dynamic disorder**

**Fitting the data**





## 2. What is XAS used for?

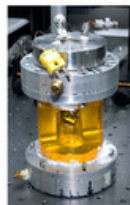
- ❑ The wiggles in the XAS data tell us something about the **atomic** and **electronic structure** of the material measured.



**Valence** the charge state of the absorber  
**Species** what kinds of atoms surround the absorber  
**Number** how many of those atoms there are  
**Distance** how far away they are  
**Disorder** thermal and structural disorder

Almost anything can go on the sample stage

XAS is usually capable of measuring your sample very close to the “proper” state  
 → in-situ



Gas flow reactor for redox chemistry



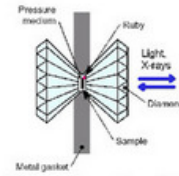
Combinatorial chemistry (Argonaut Technologies Surveyor)



Tube furnace for high-T XAS



Peristaltic pump for fluid flow



Diamond anvil cell for high-P XAS



Cryostream, bio samples (Oxford Cryosystems Cobra)

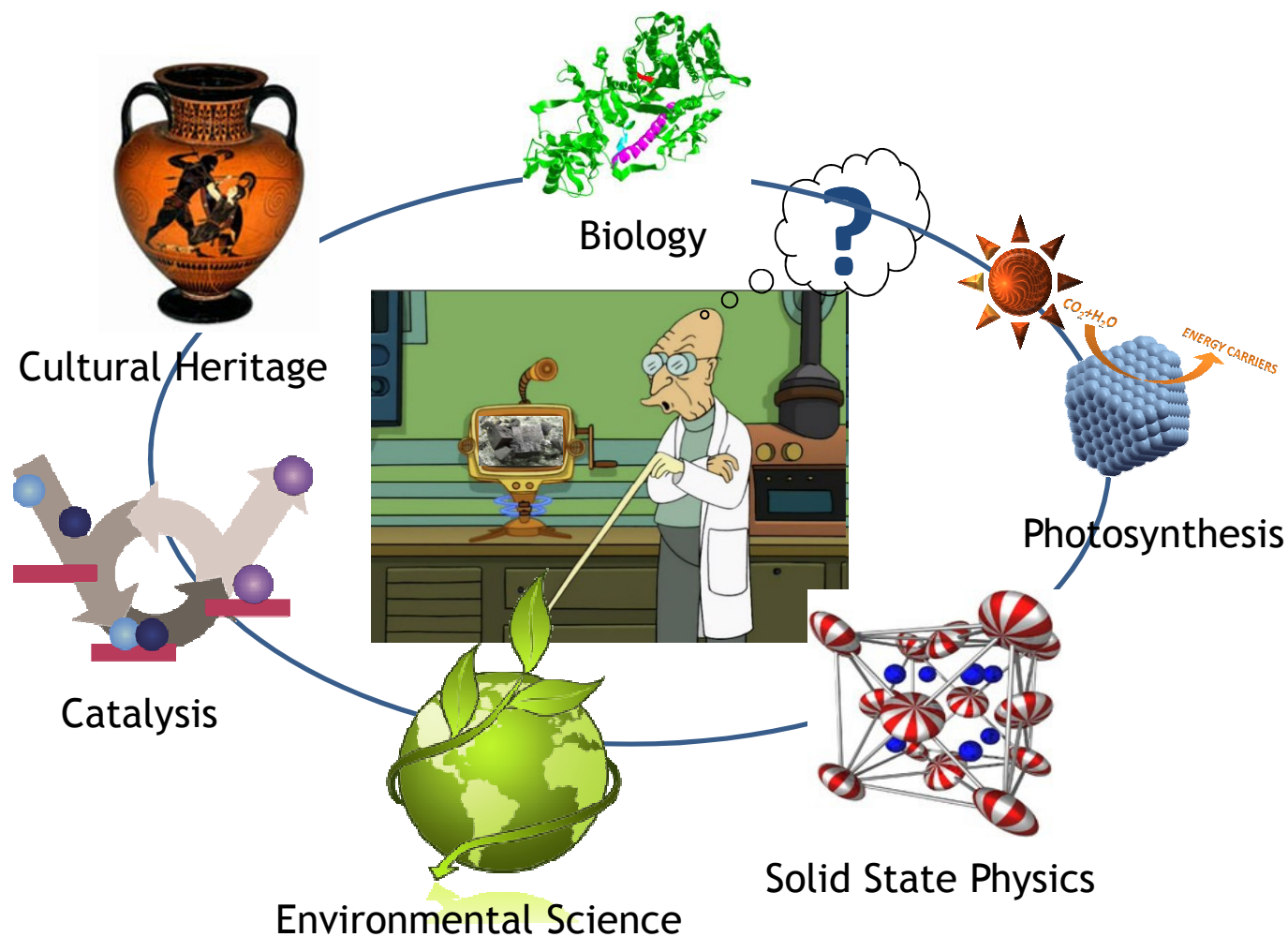


Cryostat (ARS Displex)



Tilt stage for grazing incidence

## 2. What is XAS used for?

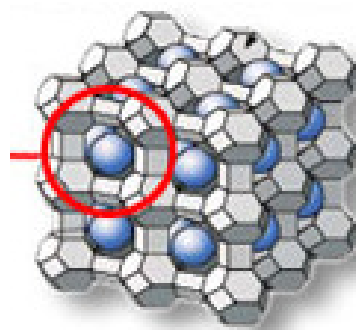
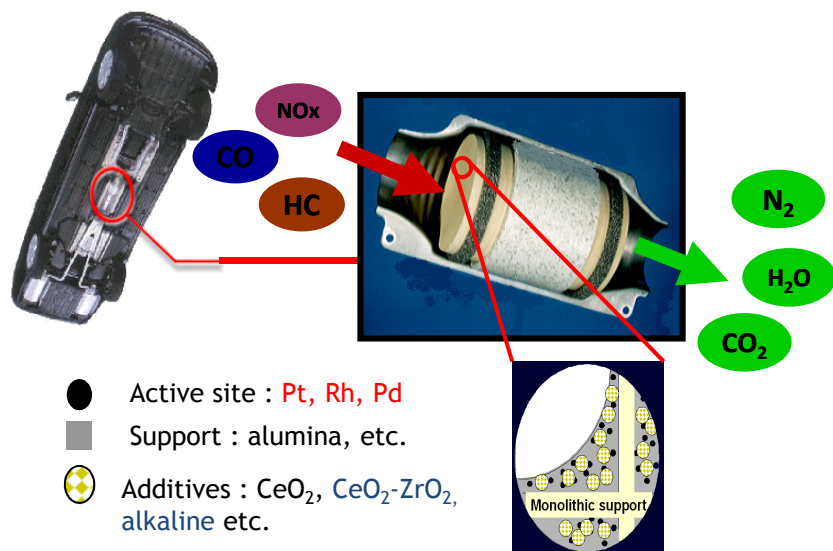


### 3. Applications

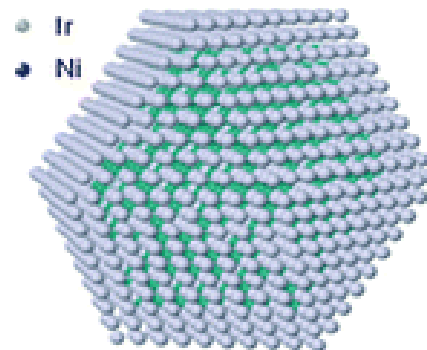
#### Catalysis

Controls 80 % world's chemical manufacturing processes

Reproduce real catalytic reaction conditions (car's exhaust pipe) to develop new catalytic converters



Structure of metal particles in a zeolite matrix in function of the pretreatment/reaction



To study the alloy formation and structure

Determination the metal particle structure of catalysts during process

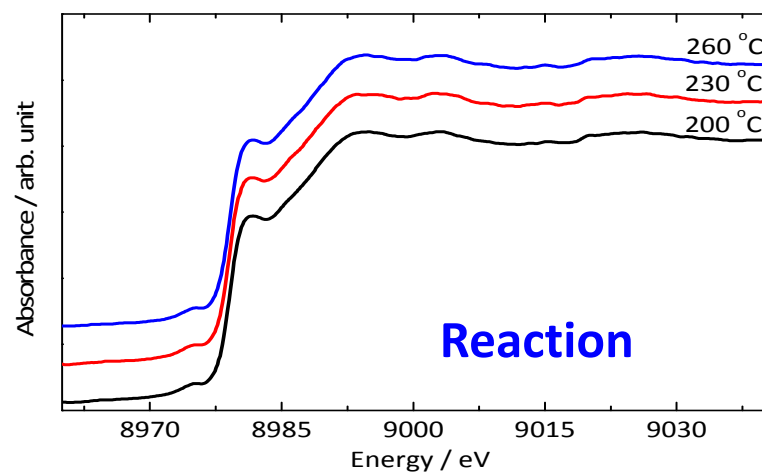
### 3. Applications

#### Catalysis at CLÆSS

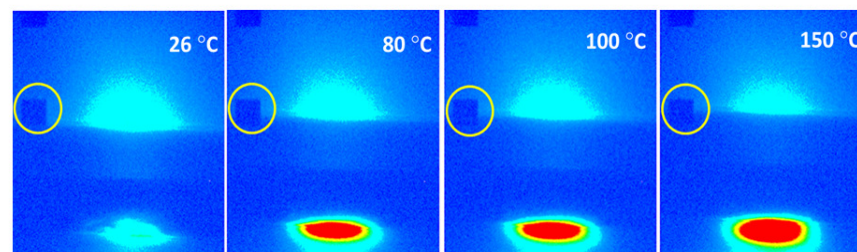
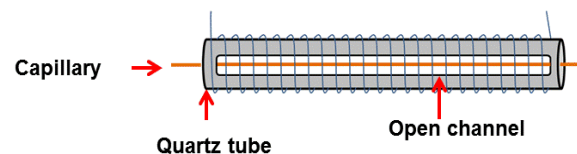
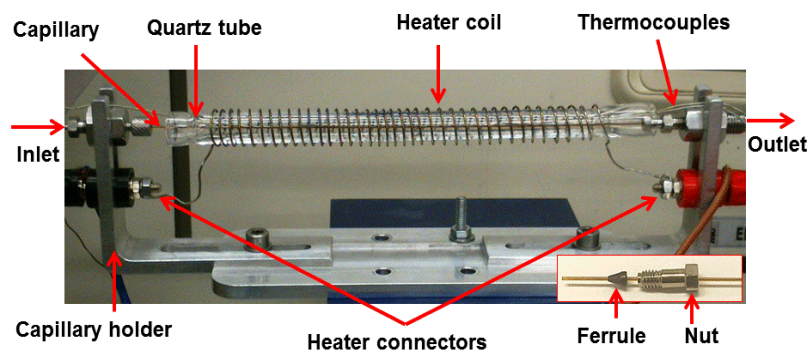


High relevance  
in C recycling

- ☐ Catalyst: Cu/Al<sub>2</sub>O<sub>3</sub> (Cu k-edge)
- ☐ Gases: 5% H<sub>2</sub>/He
- ☐ **Pressure: 200 bar**
- ☐ **Temperature: 250 °C**
- ☐ Continuous scan
- ☐ Each EXAFS scan (1200 eV) took 10 min



Cu remained at Cu(0) oxidation state under all examined conditions

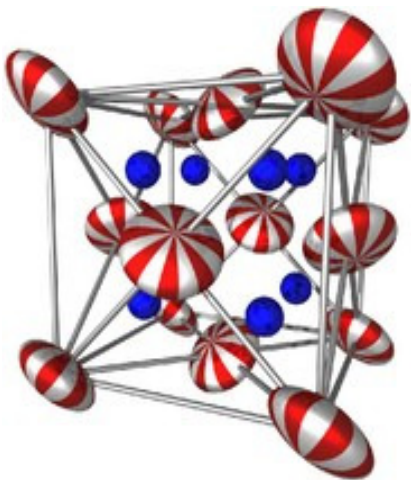


A. Bansode, G. Guiler, V. Cuartero, L. Simonelli, M. Avila and A. Urakawa, Submitted to Rev. Sci. Instrum.

## Solid State Physics

Structural changes due to phase transitions

- ☐ Temperature
- ☐ Pressure
- ☐ Magnetic Fields,...



Study of structure of batteries to extend its life and performance



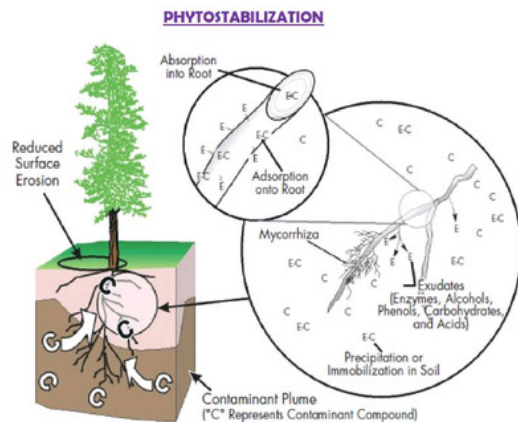


## Environmental sciences

Why speciation is so important?

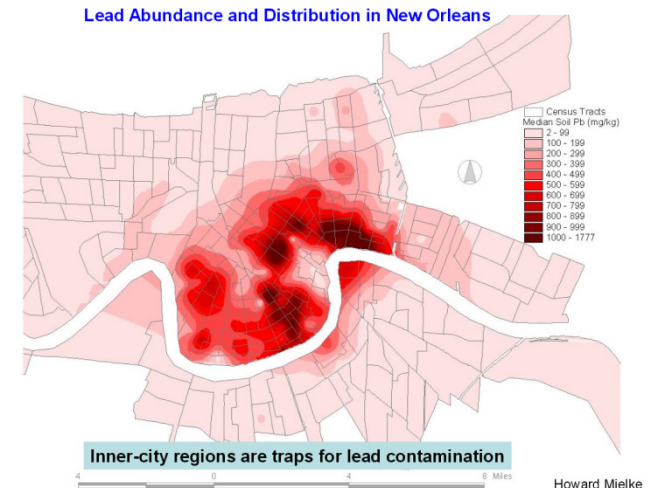


$\text{Cr}^{3+}$  is good  
 $\text{Cr}^{6+}$  is very toxic



To study the mechanisms of absorption of pollutants on plants or absorbents

- Chemical speciation controls mobility, toxicity, and bioavailability



Assess the real toxicity of polluted soils



Study of the chemical species of metals (As, Cu, Zn, ...) in food

*Anal. Chem.* 2006, 78, 7484–7492

## Blackening of Pompeian Cinnabar Paintings: X-ray Microspectroscopy Analysis

Marine Cotte,<sup>\*,†</sup> Jean Susini,<sup>†</sup> Nicole Metrich,<sup>‡</sup> Alessandra Moscato,<sup>§</sup> Corrado Gratzia,<sup>§</sup> Antonella Bertagnini,<sup>||</sup> and Mario Pagano<sup>||</sup>



Turning black. A wall painted red in the remains of Pompeii.

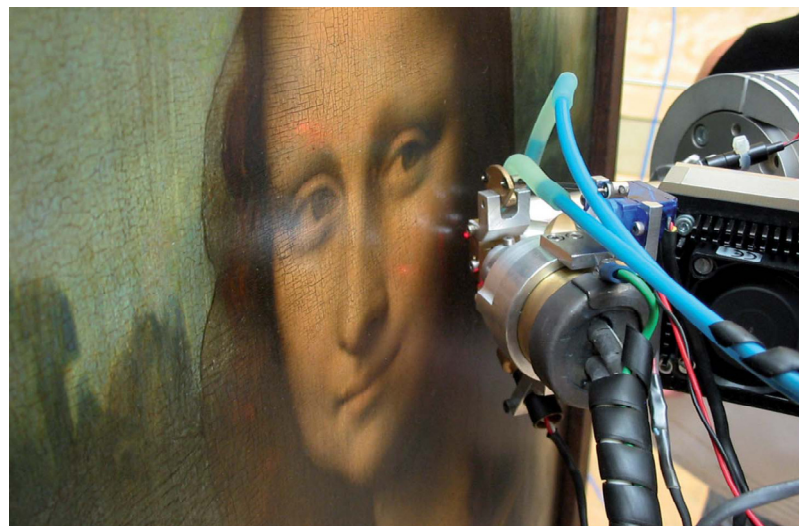
Why do the red walls of Pompei go black?

## Analyzing Works of Art

DOI: 10.1002/anie.201001116

## Revealing the *sfumato* Technique of Leonardo da Vinci by X-Ray Fluorescence Spectroscopy\*\*

Laurence de Viguerie, Philippe Walter,<sup>\*</sup> Eric Laval, Bruno Mottin, and V. Armando Solé





## 4. How can we make XAS experiments?



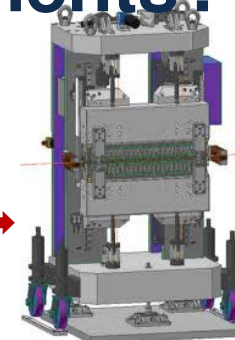
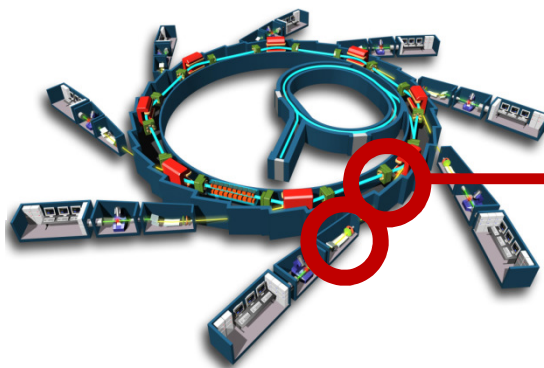
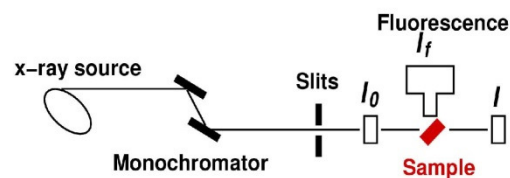
- Hard x-rays beamline  
E= 4-68 keV
- $\Delta E/E = 1.4 \cdot 10^{-4}$
- $10^{13}$  ph/s

OPTICAL HUTCH



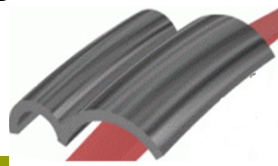
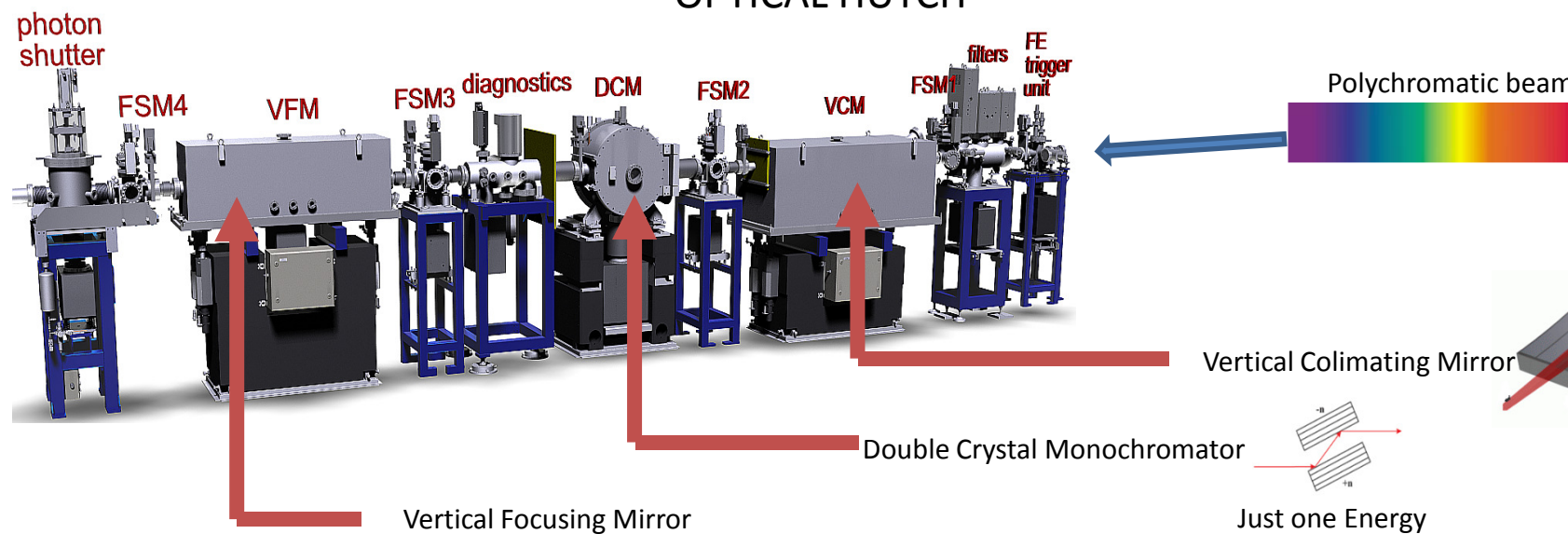
EXPERIMENTAL HUTCH

# 4. How can we make XAS experiments?

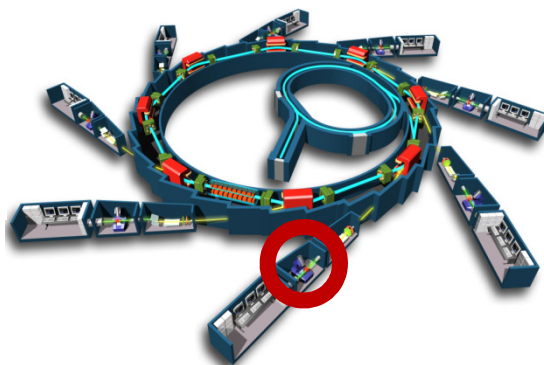
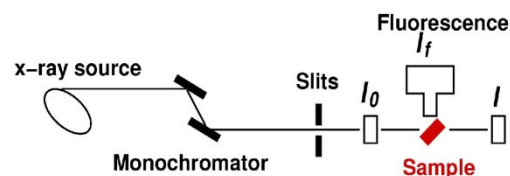


Multipole wiggler

## OPTICAL HUTCH

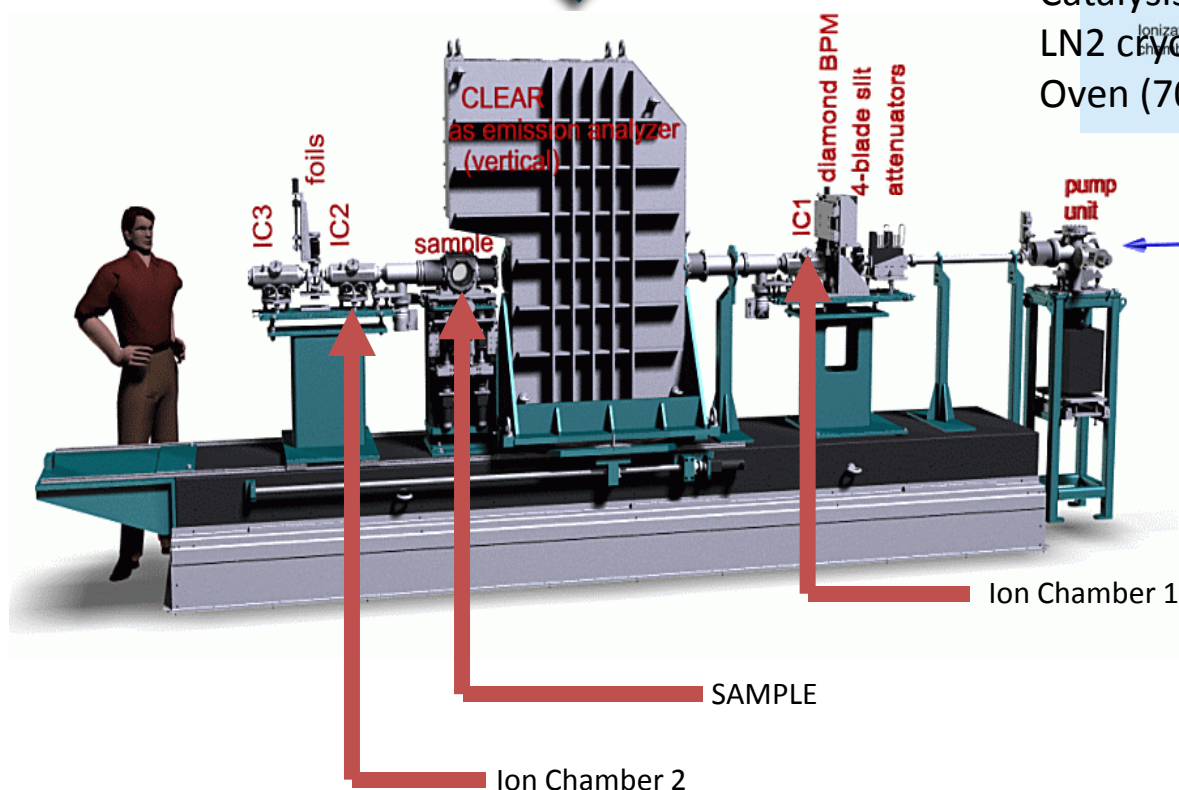
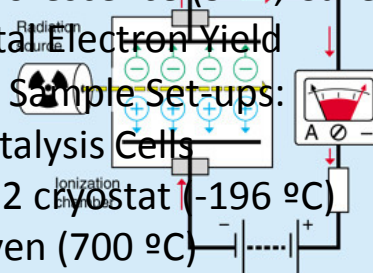


## 4. How can we make XAS experiments?



### EXPERIMENTAL HUTCH

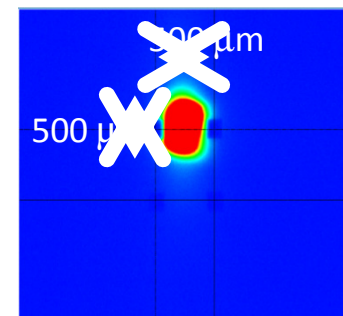
- Detection:
  - Transmission (Ion Chambers)
  - Fluorescence (SDD, CdTe, PD),
  - Total Electron Yield
- Sample Set-ups:
  - Catalysis Cells
  - LN2 cryostat (-196 °C)
  - Oven (700 °C)





## 4. How can we make XAS experiments?

1. Align the optics to the required Energy
2. Focus the beam at the sample position
3. Refill the Ion Chambers
4. Put the sample and select your detector
5. Put a reference foil



Ready to measure!



Good luck!

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## Special thanks to:

### Old and new CLÆSS team:

*Konstantin Klementiev, Gemma Guilera, Vera Cuartero,  
Laura Simonelli, Carlo Marini, Iulian Preda, Wojciech Olszewski, Marta Avila*

**Controls Engineer:** Roberto Homs

**Electronic Engineer:** José Ávila

**Mechanical Engineer:** Llibert Ribó

**Technician:** José Prieto



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**Collaborators:** Fernando Rey's group (ITQ-Valencia), Olivier Mathon (ESRF-Grenoble), Atsushi Urakawa's group (ICIQ-Tarragona), Joaquín García's group (ICMA-Zaragoza).

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**THANKS FOR YOUR  
ATTENTION!**

