INTRODUCTORY COURSE Synchrotron EXAFS & XANES for Chemical Speciation on Environmental Systems

6th - 9th October 2014

Synchrotron Applications to Biomaterials and Environment

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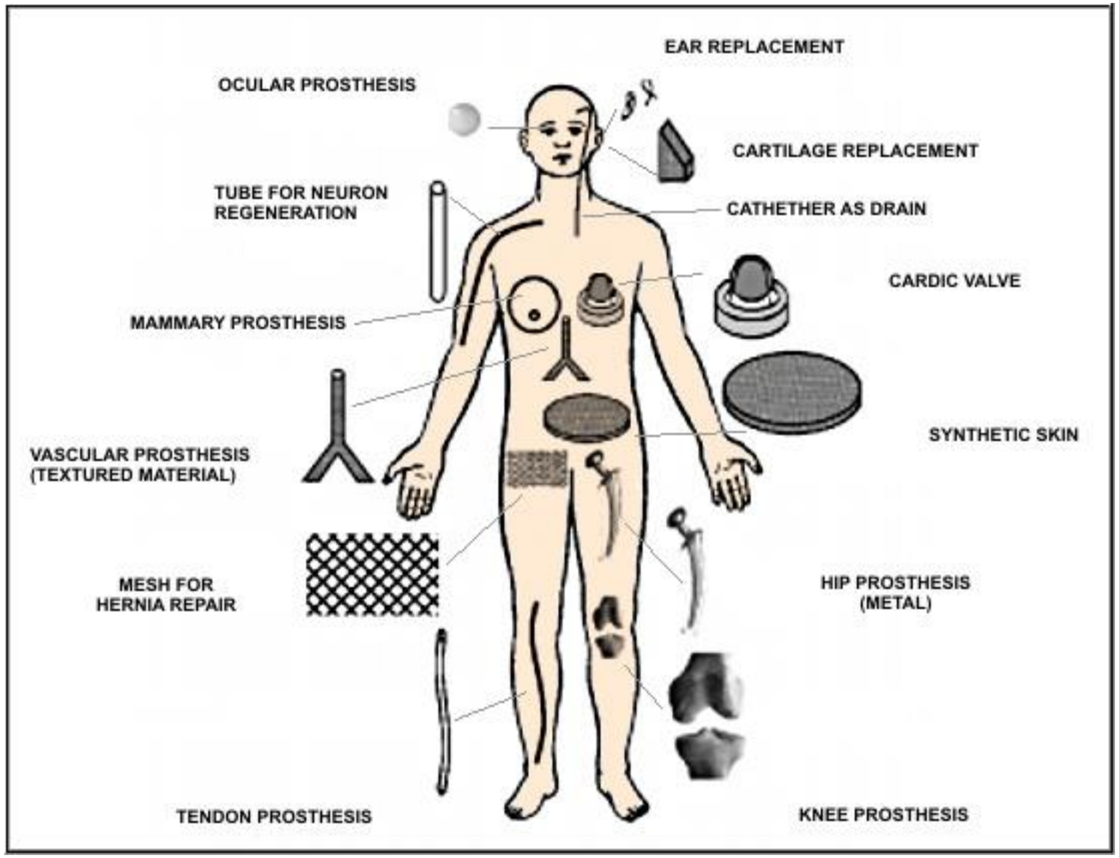
TECNIO Be tech. Be competitive

Biomaterials

are materials (synthetic and natural; solid and sometimes liquid) that are used in **medical devices** or in contact with biological systems

BIOMATERIALS



Numbers of Medical Devices/yr. Worldwide

intraocular lens	7,000,000
contact lens	75,000,000
vascular graft	400,000
hip and knee prostheses	1,000,000
catheter	300,000,000
heart valve	200,000
stent (cardiovascular)	>2,000,000
breast implant	300,000
dental implant	500,000
pacemaker	200,000
renal dialyzer	25,000,000
left ventricular assist devices	100,000

Millions of lives saved. The quality of life improved for millions more.
A $100 billion industry

ENVIRONMENT

ENVIRONMENTAL SCIENCES

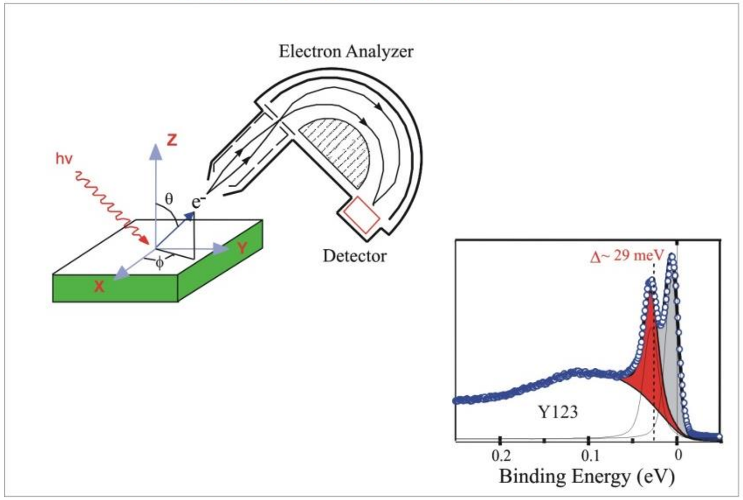
the study of the interactions among the physical, chemical and biological components of the environment

HOW?

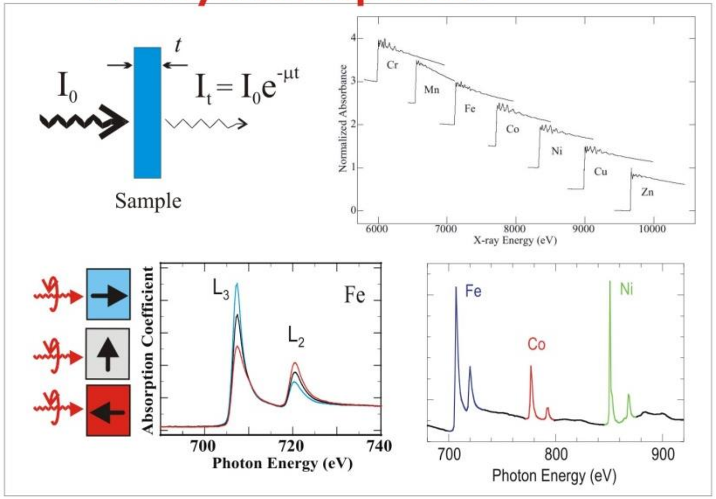
WE WILL USE PHOTONS

Photons Enable a Range of Modern Techniques to Study Matter

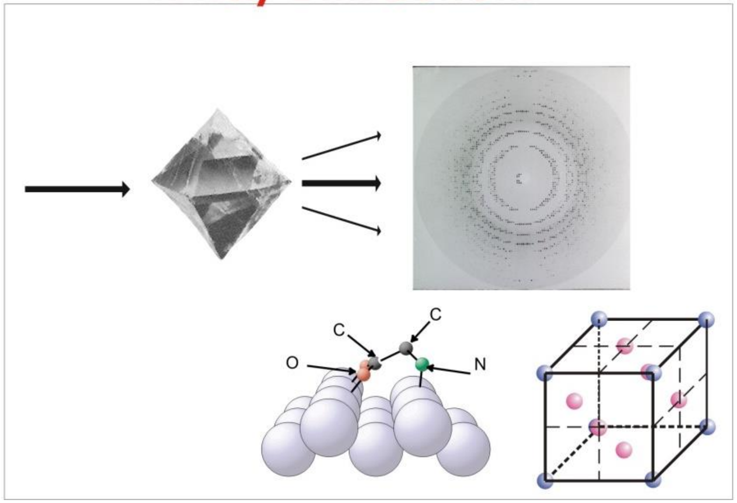
Photoemission:



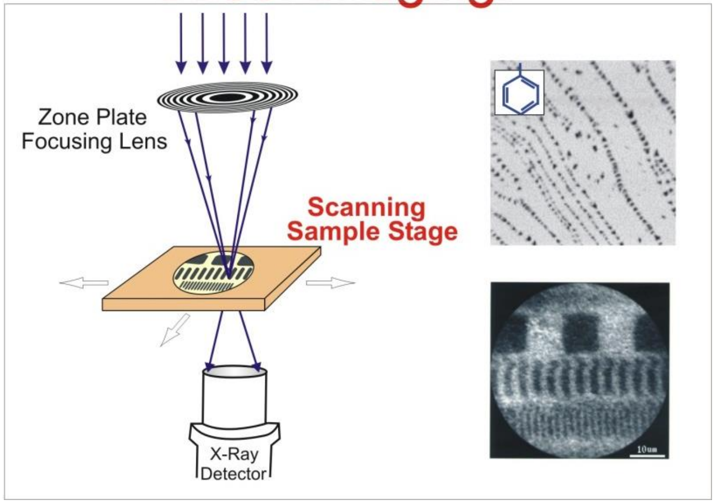
X-Ray Absorption:



X-Ray Diffraction:



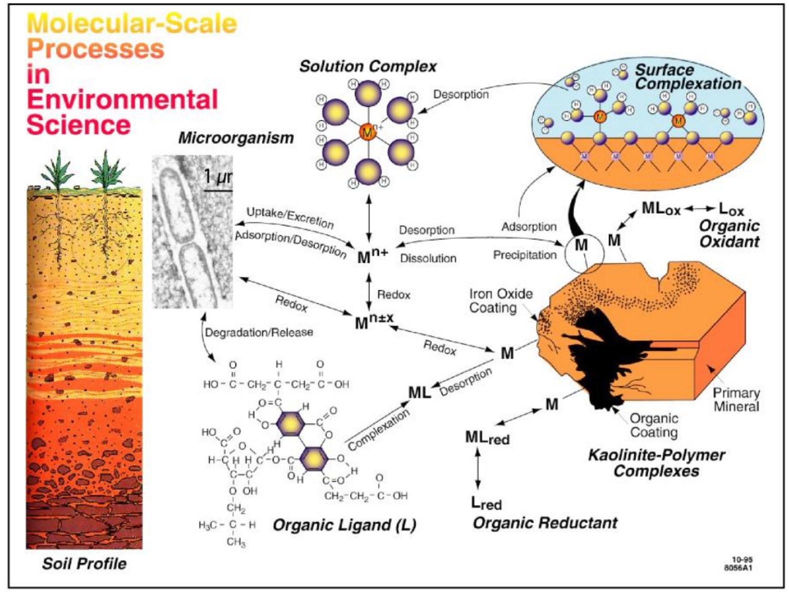
Direct Imaging:



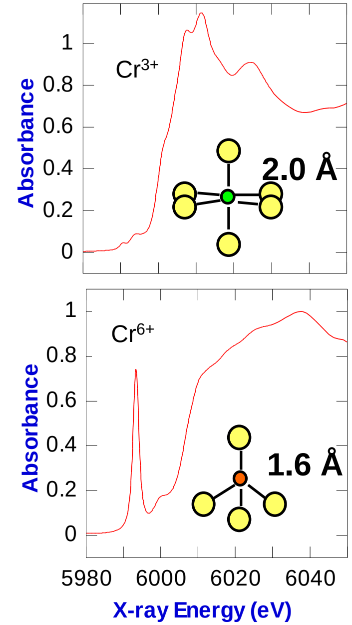
Some Key Issues in Molecular Environmental Science

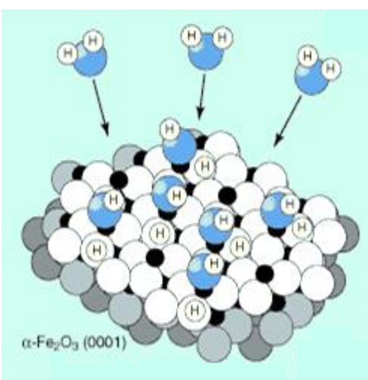
Water and Interfaces

Complexity

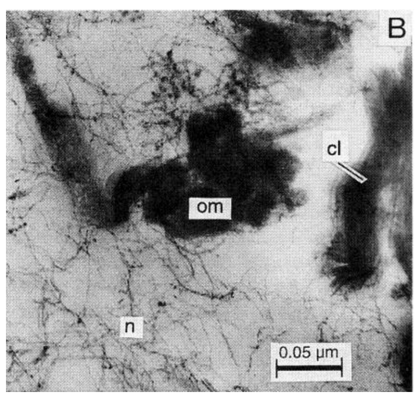


Speciation

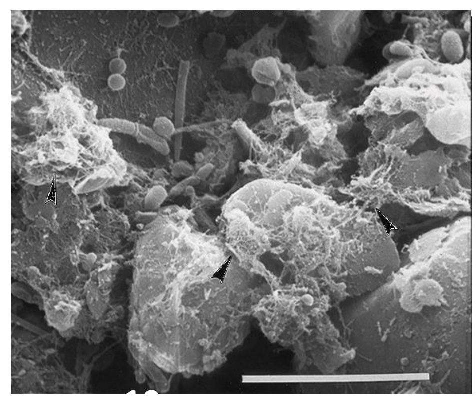




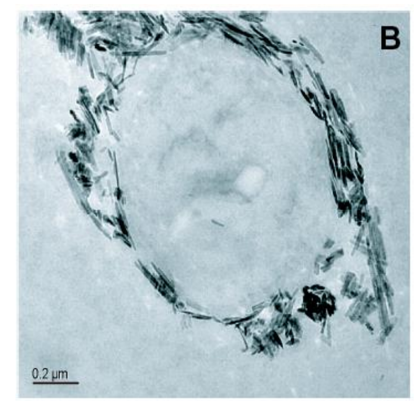
Surface Reactions



Natural Organic Matter



Microorganisms & Biofilms



Nanoparticles

EXAMPLE

ENVIRONMENT

BIOMATERIAL

Widespread in the environment

Highly toxic for human beings and biota

Significant **bioaccumulation** through food chain

Potential hazard for the <u>environment</u> and <u>human beings</u>

Chemical form

Chemical speciation

Toxicity of Mercury

- **Likelihood of exposure**

- **Geochemical and environmental factors** (redox potential, pH, reaction kinetics, soil type (sorbing materials: clays, Fe/Mn oxides and organic matter), etc.)

- **Speciation.** Toxicity (as well as mobility and bioavailability) strongly dependent on the chemical form in which mercury is found

alkyl Hg (e.g. CH_3Hg^+) **>** Hg metal vapour, Hg^{2+} salts

Toxic effects on the physiological and the neurological systems. Methylmercury effects on the central nervous system are the most destructive

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Application of X-ray Synchrotron-Based Techniques to the Study of the Speciation of **Hg** in Environmental and Biological Systems

HASYLAB

ESRF

LELAND STANFORD JUNIOR UNIVERSITY
ORGANIZED 1891

Hg production

Primary production
(mining extraction)

- Main element
- By-product (gold-silver and massive sulphide deposits)

Secondary production
(recycling, recovering, reuse)

- Dismantling of chlor-alkali plants
- Recovery from Hg counters
- Recovery from rectifiers and Hg manometers

Uses of mercury

-Extractant in gold and silver production

-Mercury-cathode for chlor-alkali industries

-Discharge lamps

-Power rectifiers

-Mercury batteries

-Thermometers

-Barometers

-Electrical switches

-Laboratory products

-Dentistry (dental amalgam)

-etc.

Increasing social awareness ➡ **Drop in industrial applications** ➡ **Substitution of Hg products**

Dental amalgam

Almadén mine

Largest and oldest in the world

Mining activity ceased in 2002

Impressive legacy of contamination

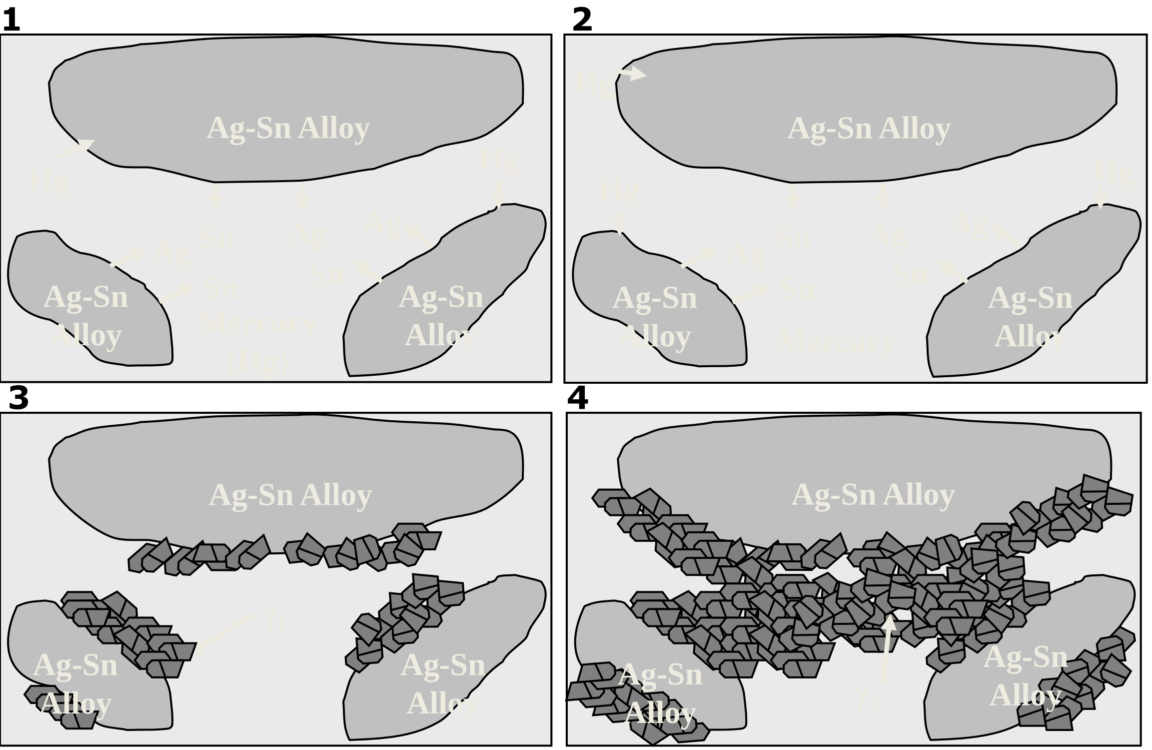
Dental amalgams[3]

Known since more than 150 years

Chemical composition: Hg (l) + Ag/Sn/Cu (Zn/Pb/In/Se)

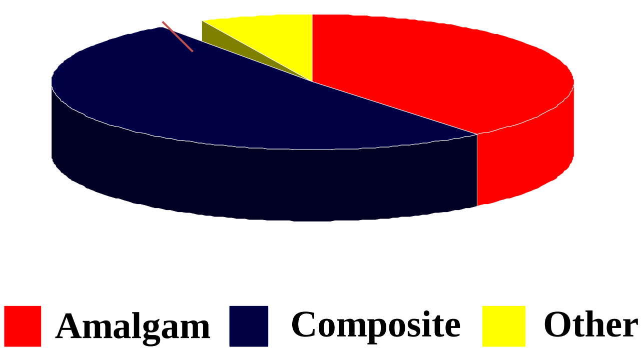
Amalgamation process:

$$\underset{\gamma}{Ag_3Sn} + Hg \Rightarrow \underset{\gamma}{Ag_3Sn} + \underset{\gamma_1}{Ag_2Hg_3} + \underset{\gamma_2}{Sn_{7\text{-}8}Hg}$$ [4]



Highly successful material: high resistance and cost effective

Social awareness about its biocompatibility. Alternatives:



[3] Craig, R.G.; Powers, J.M. *Restorative dental materials*, Eleventh edition. Elsevier Health Sciences, St. Louis, 2002

[4] Phillip's Science of Dental Materials. 11th Ed. W.B. Saunders, 2003. USA

Speciation methods

The number and reliability of analytical techniques is limited

Conventional methods

- -Extraction (distillation/ solvent extraction/ supercritical fluids)
- -Separation (GC, HPLC, CE, etc.)
- -Detection (UV, ICP-OES, CV-AAS, etc.)

Drawbacks: Risk of species modification

Limited amount of detectable species (mainly organometallic forms of Hg)

Other approaches:

Theoretical approaches: use of thermodynamic data to assess chemical speciation

Thermal desorption: speciation according with their decomposition temperatures

X-ray diffraction: identification of crystalline structures in the sample

XAS techniques

X-ray absorption techniques[9,10,11]

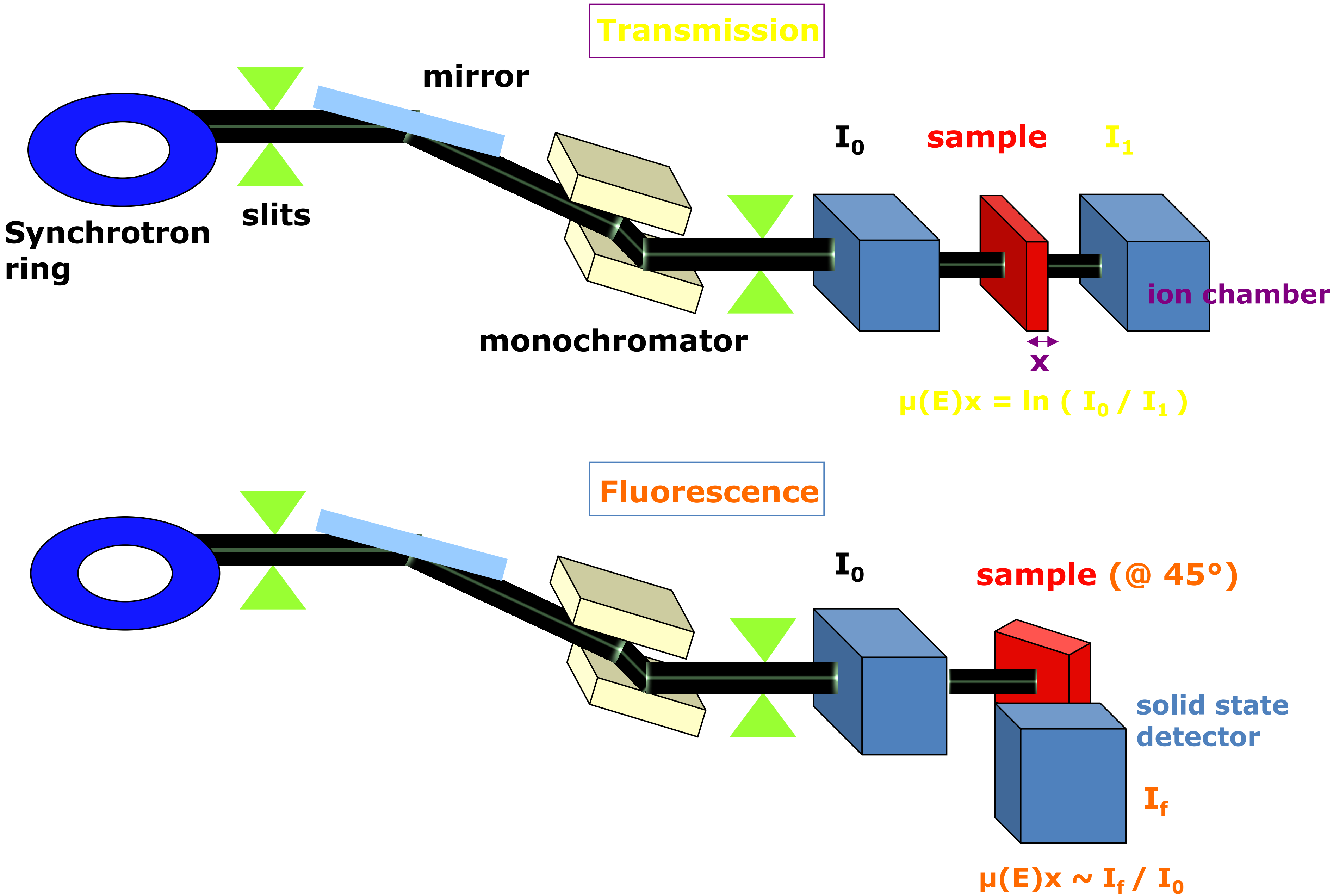
Interesting and readily available tool to overcome the existing speciation gap

Study the elemental specific local atomic structure, based on the interaction between the sample and a X-ray radiation provided by a synchrotron facility

[9] Brown Jr., G.E. et al. X-ray Absorption Spectroscopy and its Applications in Mineralogy and Geochemistry. Hawthorne, F.C. (ed.), Vol. 18, Chap. 11, Washington, 1988

[10] Stern, E.A.; Heald, S.M. X-Ray Absorption. Principles, applications, techniques of EXAFS, SEXAFS and XANES. Koningsberger, D.C.; Prins, R. (eds.), John Wiley & Sons, New York, 1988

[11] de Groot, F. et al. Neutron and X-ray Spectroscopy. Hippert, F. et al. (eds.), Springer, Dordrecht, 2006


Transmission
mirror
slits
Synchrotron ring
monochromator
I0
sample
I1
ion chamber
x
μ(E)x = ln (I0 / I1)
Fluorescence
I0
sample (@ 45°)
solid state detector
If
μ(E)x ~ If / I0

Objectives

Mercury speciation in environmental and biological samples to assess their influence on the specific behaviour of Hg

- **Application of the gained know-how to the study of highly Hg-impacted environments. Assesment of Hg mobility and bioavailability:**
  - ✓ mine environments

- **Study of mercury behaviour in human teeth restored with dental amalgams**
  - ✓ microprobe techniques to assess diffusion processes and study the molecular environment of Hg


Complex Process
We are here

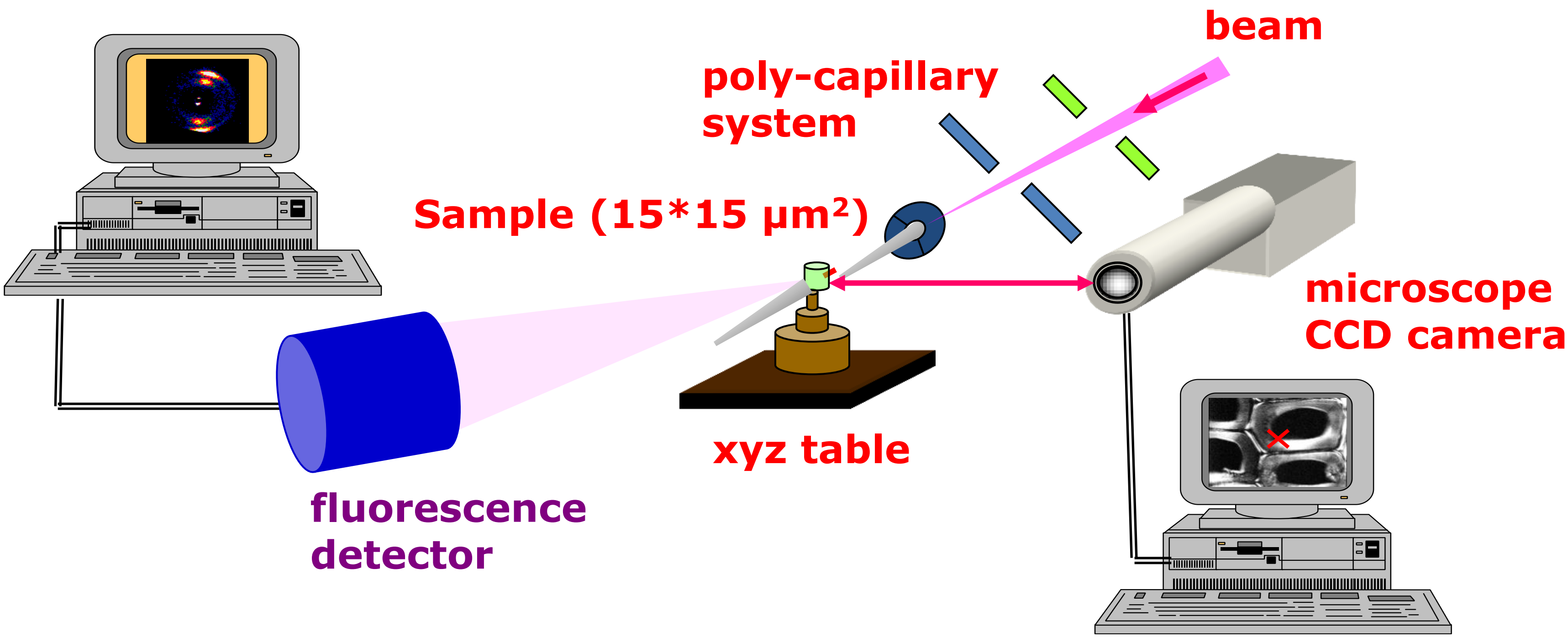
Hg mine Almaden

Dental amalgam

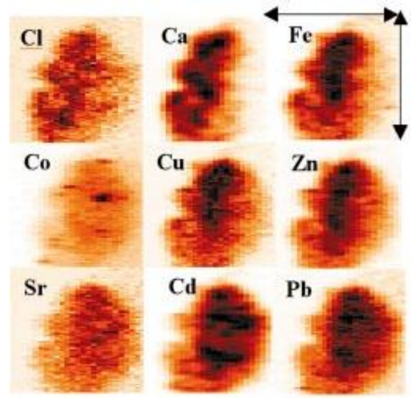
Hg-impacted environments

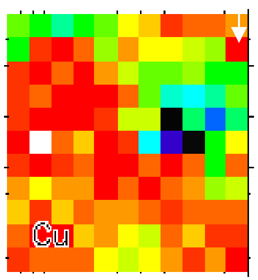
- ✓ **Sample preparation and characterization**
- ✓ **XAS analysis – data treatment**
- ✓ **Complementary techniques:**
  - **SES**
  - **SEM-EDS**

XAS techniques – spatial resolution at micro-scale level



μ-XRF[13]
- map elemental distributions by step-scan mode
- simultaneous multi element trace analysis



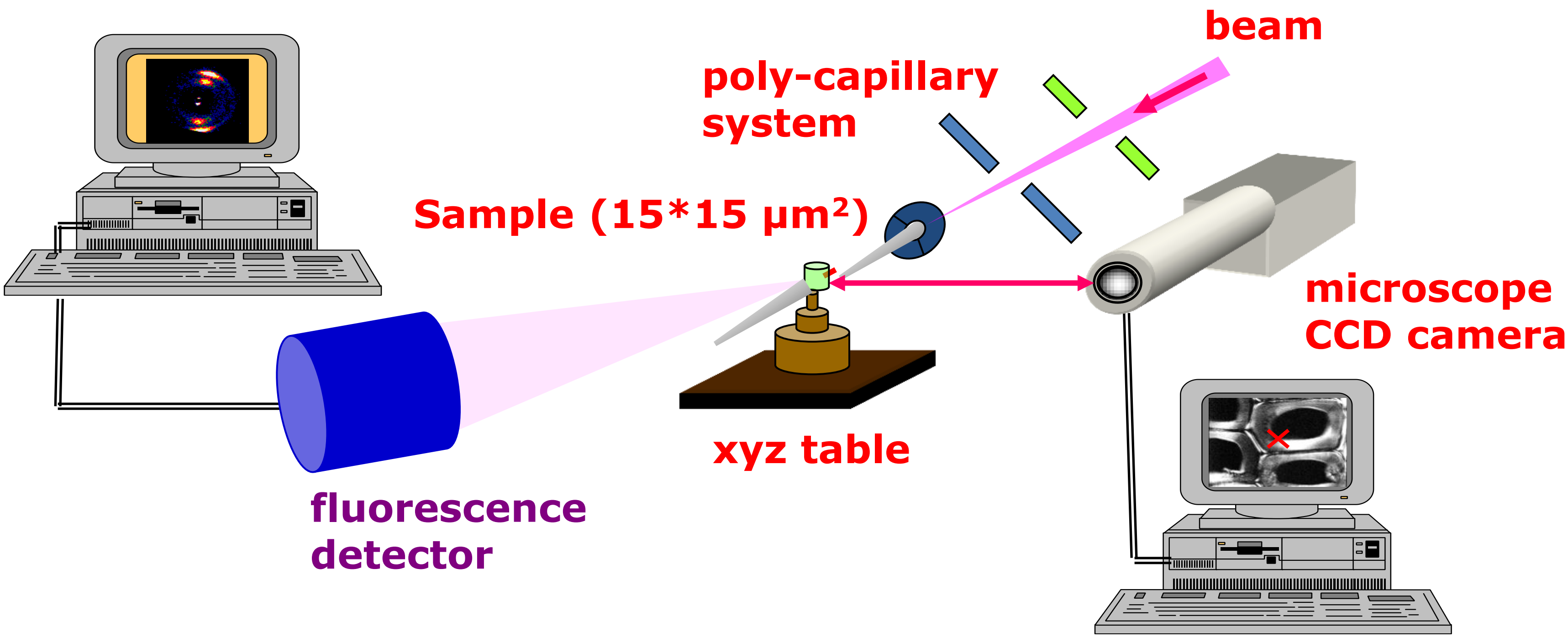


121 pixel

10 μm

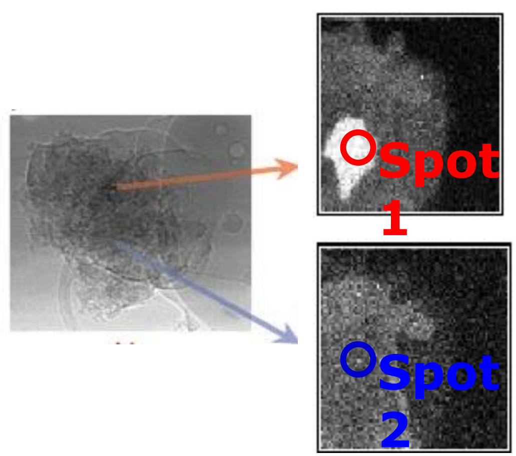
[13] Camerani, M.C.; Somogyi A.; Drakopoulos M. et al. Spectrochimica Acta Part B, 2001, 56, 1355-1365

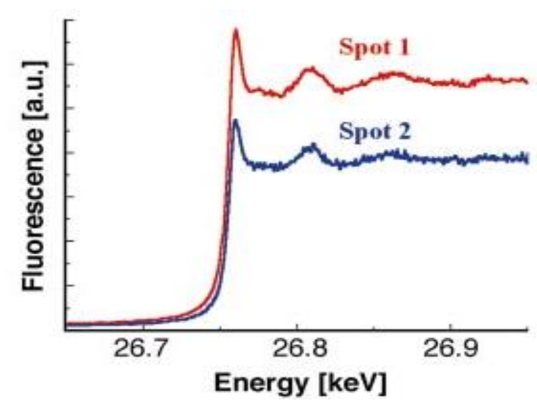
XAS techniques – spatial resolution at micro-scale level



μ-XAS[13]

- Higher Hg concentration
- No interfered matrix effect





[13] Camerani, M.C.; Somogyi A.; Drakopoulos M. et al. Spectrochimica Acta Part B, 2001, 56, 1355-1365

➢ Sample preparation and characterization

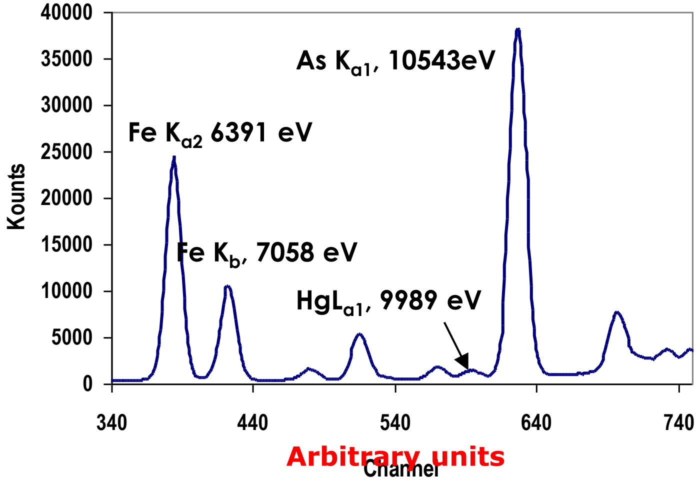
- Collection of samples

Almadén mining area: ore, soil, slag and calcine samples

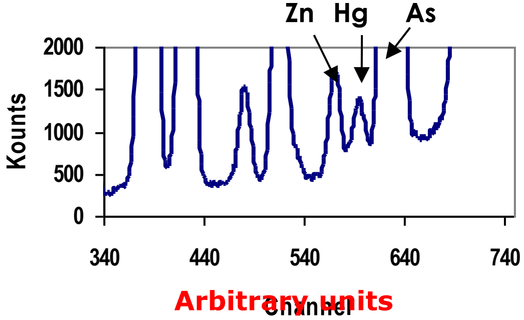
- Dried, milled, homogenized and sieved under 100 µm

- MW digestion and total metal content (Hg, As, Cu, Zn, Ni, Pb, Fe, Mn) by ICP-OES

XRD



SEM-EDS



Experimental

Hg-impacted environments

➢ Sample preparation and characterization

➢ XAS analysis

ESRF (beamline ID26) ➡ XANES

HASYLAB (beamline A1) ➡ XANES

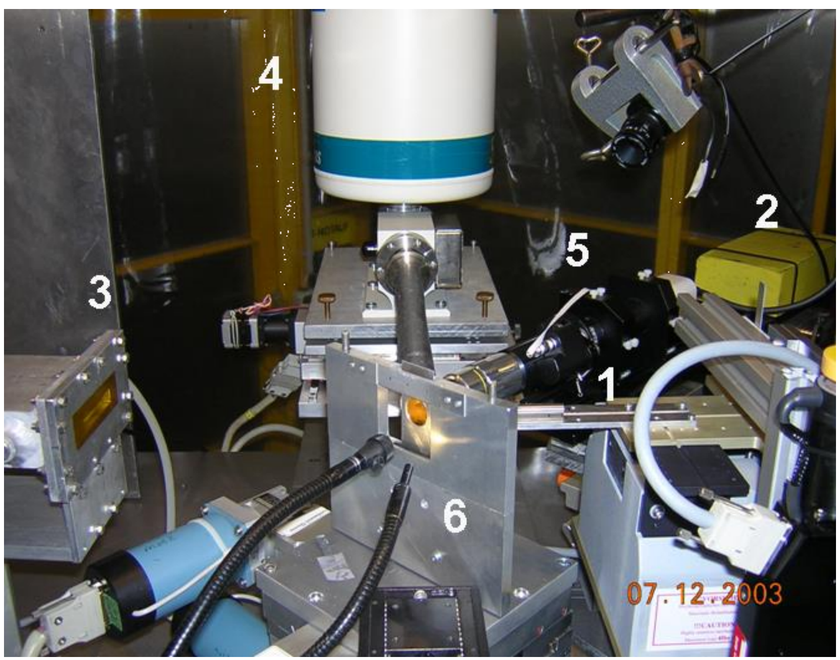
(beamline L) ➡ μ-XANES, μ-EXAFS, μ-XRF

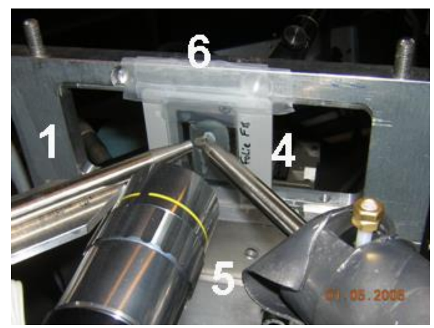
Transmittance mode; L_{III} (12284 eV)

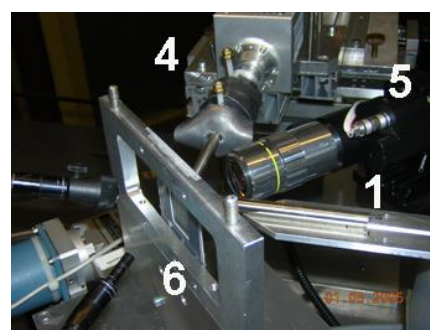
reference compounds **($HgCl_2$, Hg_2Cl_2, $HgSO_4$, HgO, $Hg(CH_3COO)_2$, CH_3HgCl, cinnabar, metacinnabar, C_6H_5HgCl, mosesite, corderoite, terlinguaite, schuetteite)**

Fluorescence mode; $L_{\alpha1}$ (9988.8 eV), $L_{\alpha2}$ (9897.6 eV)

unknown samples



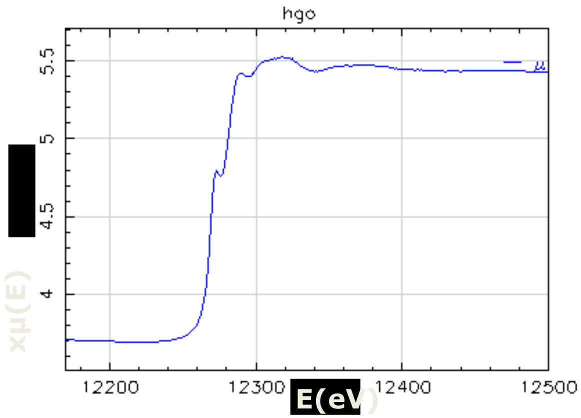




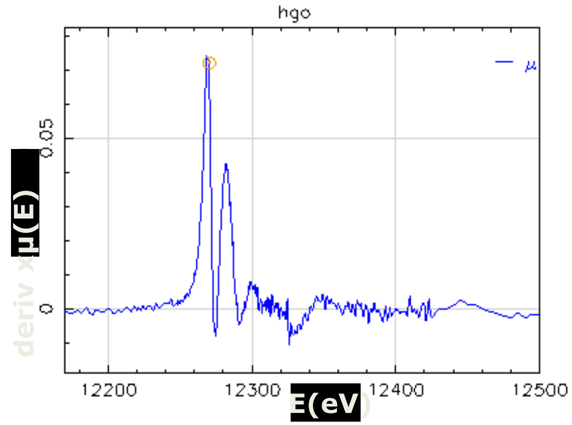
1. **Polycapillary halflens**
2. **Ionisation chamber 1**
3. **Ionisation chamber 2**
4. **Fluorescence detector**
5. **CCD-camera**
6. **Sampler**

➢ XAS analysis - data treatment: WinXAS[18] and SixPACK[19] software

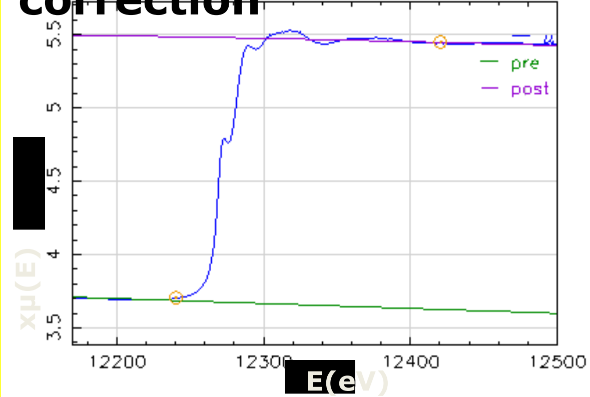
raw data



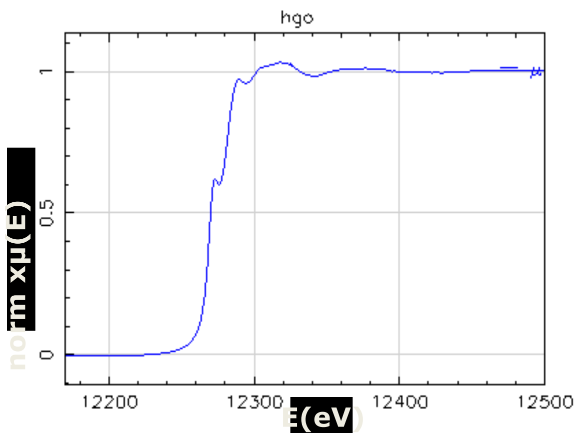
1. Energy calibration



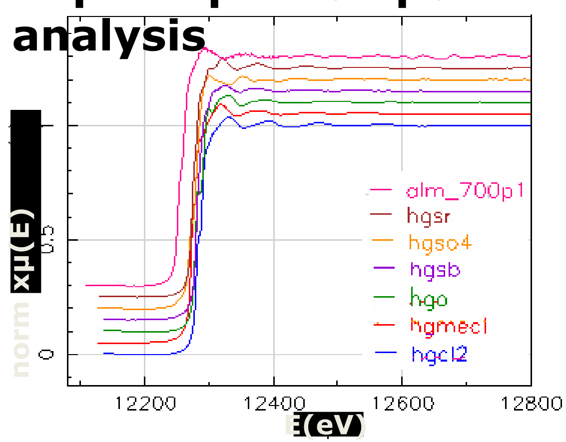
2. pre- post- edge bg correction



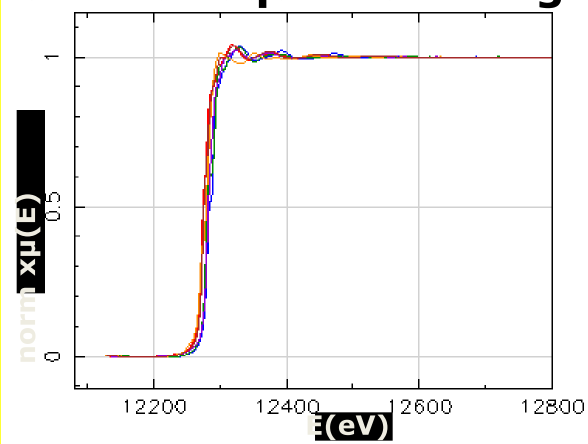
3. edge normalization



4. principal component analysis



5. least-squares fitting



[18] Ressler, T. Journal of Synchrotron Radiation, 1998, 5(2), 118-122
[19] Newville, M. SIXPack (Sam's Interface for XAS analysis Package), IFEFFIT 1.2.6, University of Chicago, 2004

DENTAL TISSUES

Experimental

➢ Sample preparation and characterization

- Sixteen amalgam containing human molar teeth from clinical offices
- rinsed, disinfected

- thin longitudinal slices ⟶ microprobe analysis

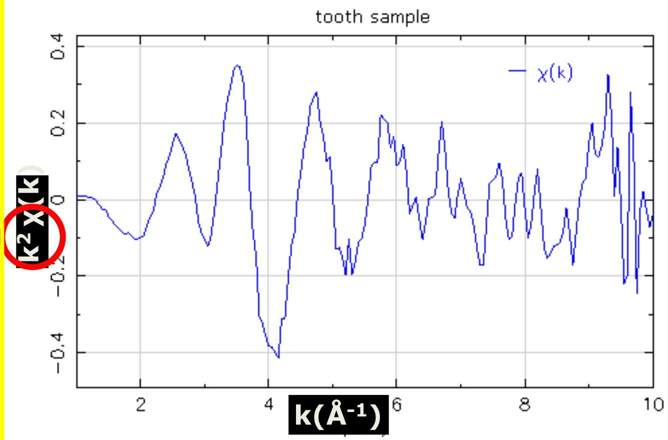
- SEM-EDS: first qualitative overview on the elemental composition

➢ XAS analysis

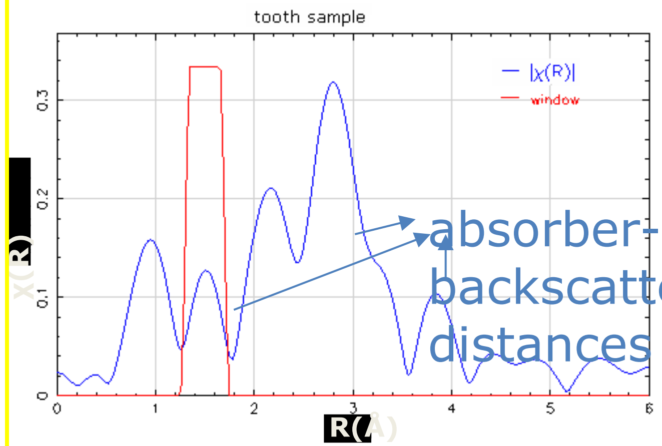
HASYLAB (beamline L):
- μ-XRF (Ca, Hg, Fe, Mn, Cu, Pb, Zn, Br)
- μ-EXAFS, Fluorescence mode; $L_{\alpha 1}$ (9988.8 eV), $L_{\alpha 2}$ (9897.6 eV)

➢ XAS analysis - data treatment: (µ-EXAFS)

6. Conversion k



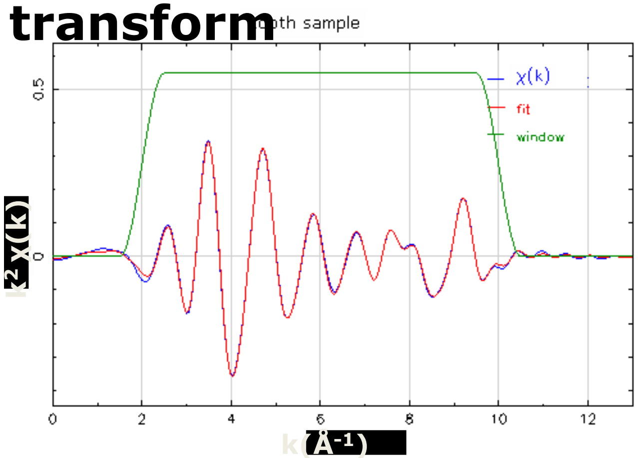
7. Fourier



radial distribution function

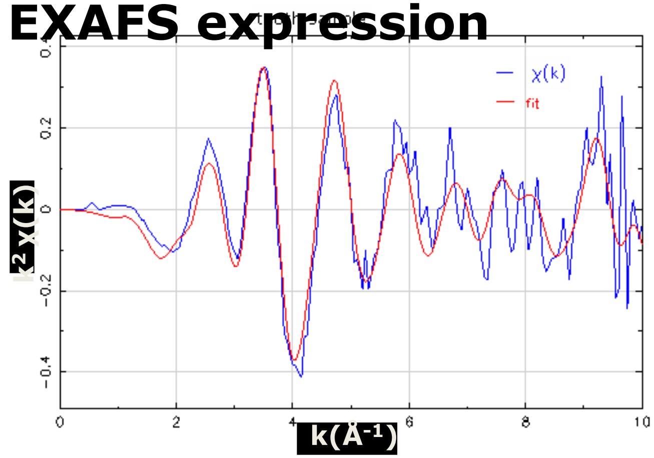
absorber-backscatterer distances

8. Inverse Fourier transform



structural parameters each shell

9. Least-squares fitting EXAFS expression



N_j, nº neighbours
R_j, distance
σ_j, Debye-Waller factor

Results

Almadén mine environment

4. Results and Discussion

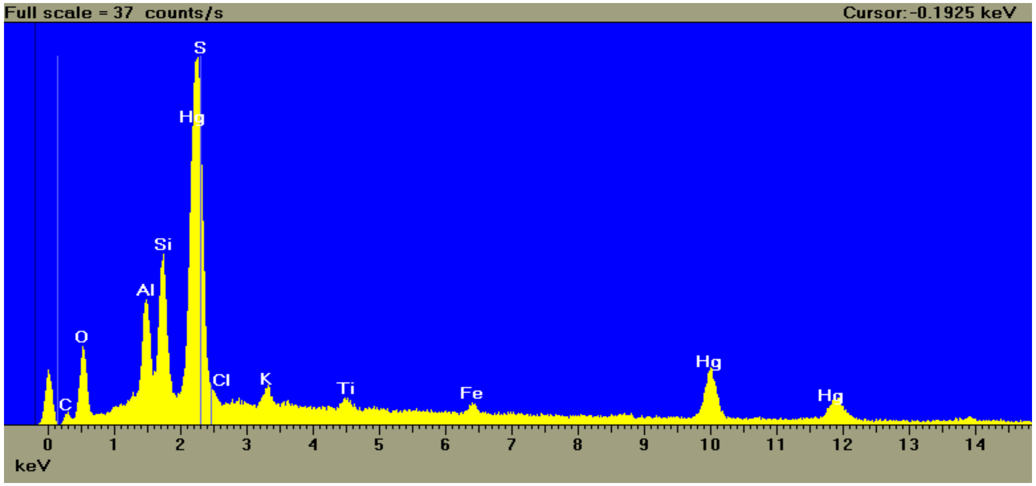
Almadén mine environment

Total metal content (ppm) by MW digestion + ICP-OES

	Hg	As	Zn	Cu	Ni	Pb	Fe ($g \cdot Kg^{-1}$)	Mn
ore 1	39000±1000	430±40	185±6	< 1	1700±300	260±40	52.4±0.4	600±10
ore 2	33000±3000	470±9	< 1	< 1	1400±100	290±20	50±2	540±10
ore 3	41000±3000	490±10	< 1	< 1	1580±50	278±5	53±4	639±7
ore 4	28900±800	500±8	280±10	< 1	1580±80	295±2	51.6±0.8	553±2
ore 5	38600±300	450±70	< 1	< 1	1500±100	260±40	49.9±0.2	632±3
soil 1	630±30	290±50	< 1	< 1	670±10	< 1	43±1	< 1
soil 2	1080±30	320±30	< 1	< 1	950±90	260±20	51.0±0.5	460±10
soil 3	1090±30	340±10	< 1	< 1	960±60	229±7	44±3	510±10
soil 4	1200±100	340±20	< 1	< 1	1000±200	208±6	51±2	420±20
soil 5	1450±30	310±6	< 1	< 1	860±30	< 1	44±1	< 1
soil 6	400±10	320±20	< 1	< 1	1008±6	< 1	37.1±0.2	330±10
soil 7	840±20	310±30	< 1	< 1	1160±20	220±30	40.9±0.2	632±6
soil 8	1820±10	340±40	< 1	< 1	1100±200	210±20	41.9±0.7	301±6
soil 9	1360±50	310±20	< 1	< 1	1100±100	< 1	40.2±0.4	640±10
soil 10	1720±10	320±5	310±30	< 1	1260±90	287±8	47.5±0.3	390±10
slag 1	460±30	320±20	< 1	< 1	1410±40	< 1	61.7±0.5	< 1
slag 2	380±6	300±10	390±10	65±1	1290±80	< 1	78.96±0.04	< 1
slag 3	240±3	340±40	< 1	73±1	1400±200	206±7	86.4±0.8	< 1
calcine 1	35000±6000	< 1	2200±400	33±7	36±6	91±13	70±16	280±60
calcine 2	6700±500	< 1	2500±200	33±2	41±2	276±190	65±2	798±8

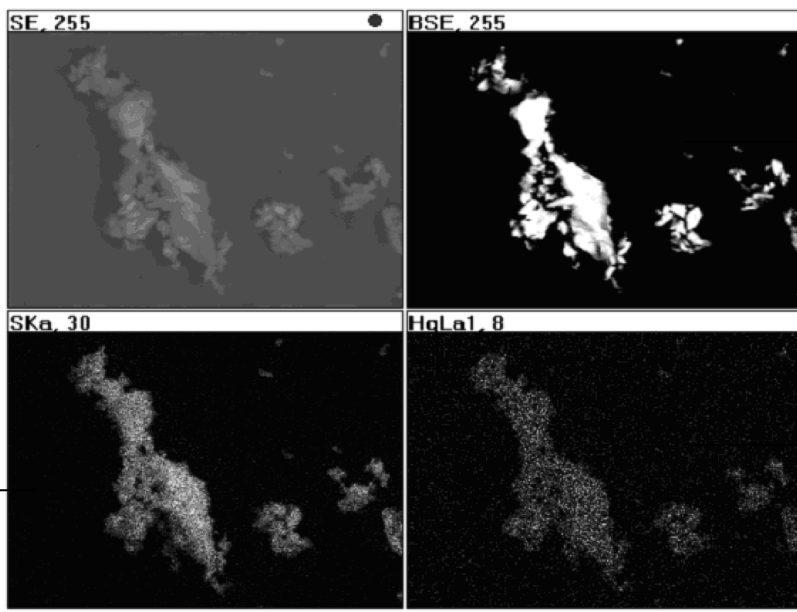
ESRF: high excitations of Fe and saturation of the fluorescence detector

SEM-EDS analysis ➡ compositional information of the bulk



Full-field area ➡ clay composition (Al, Si, K and Fe)

Results corroborated by XRD



Hg rich particle

Clear association between Hg and S

K_αS (2307.8 eV)

L_αHg (9988.8 eV)

Speciation results by XANES, μ-XANES and μ-EXAFS

Sample	HgS_{red}	HgS_{black}	$HgSO_4$	$HgCl_2$	HgO	Schuetteite	Residual
ore 1	77	12	6	6	<3		0.025
ore 2	54	19	14	6	5		0.059
ore 3	51	9	6	29	4		0.047
ore 4	63	10	8	14	4		0.054
ore 5	68	7	6	14	5		0.035
soil 1	66	<3	14	<3	17		0.218
soil 2	56	<3	22	22	<3		0.186
soil 3	41	<3	24	19	16		0.282
soil 4	74	<3	14	<3	10		0.178
soil 5	66	<3	17	18	<3		0.149
soil 6	34	<3	5	47	14		0.111
soil 7	64	<3	18	18	<3		0.191
soil 8	62	<3	20	19	<3		0.155
soil 9	54	<3	21	25	<3		0.160
soil 10	76	<3	24	<3	<3		0.195
slag 1	<3	88	12	<3	<3		0.126
slag 2	10	65	18	<3	7		0.172
slag 3	29	42	16	12	<3		0.122
calcine1; p.1	<5				47	49	0.17[b]
calcine1; p.2	34				41	24	0.74[b]
calcine1; p.3	9				55	36	0.26[b]
calcine2; p.1	89				5	6	0.23[b]
calcine2; p.2	26				47	27	1.68[b]
calcine2; p.3	14				38	47	1.32[b]

[b] evaluated by the reduced chi square value (χ^2)

▪**Cinnabar:** main Hg species in ore and soil samples

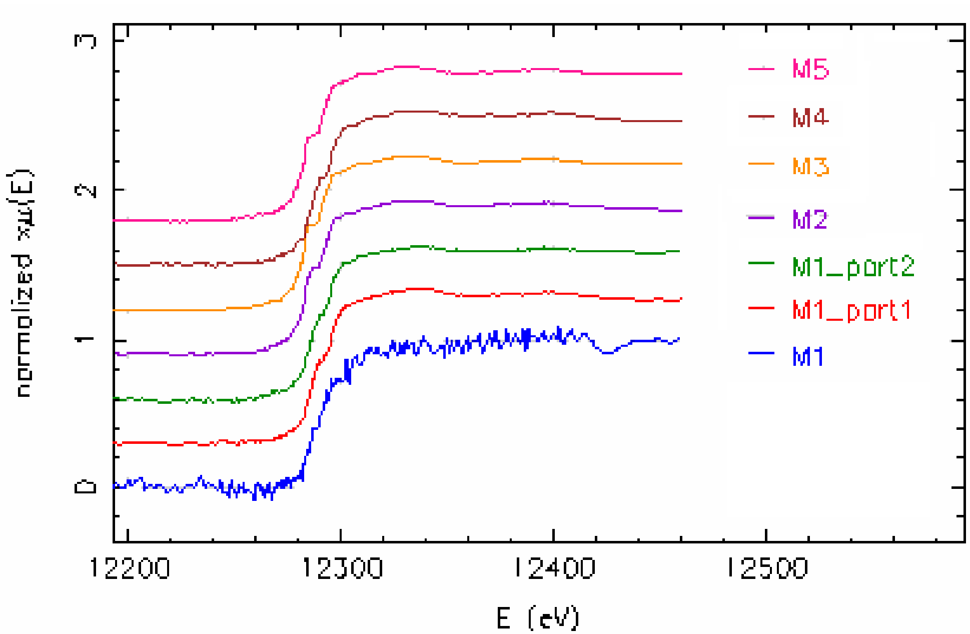
▪**Metacinnabar:** main Hg species in slags. No appear in calcine samples

▪**HgO:** slow conversion of HgS under aerobic conditions

▪**Schuetteite:** supergene alteration of cinnabar, on sunlight-exposed rocks

▪**$HgSO_4$, $HgCl_2$:** decomposition of hydrothermal alteration products or exposure of Hg ores and slags to weathering processes

Speciation results by XANES and μ-XANES



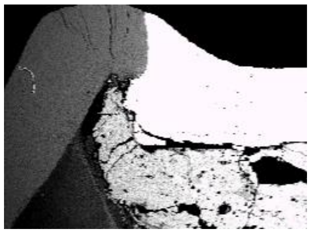
- Sample bulk: predominance of cinnabar and corderoite
- $HgSO_4$, HgO identified in significant proportions ➡ risk of Hg mobilisation
- Environmental conditions:
  - presence of S ➡ HgS
  - HgS oxidation in surface, oxygenated soils or wastes ➡ $HgSO_4$, HgO
  - NaCl used as raw material in chlor-alkali plant ➡ corderoite

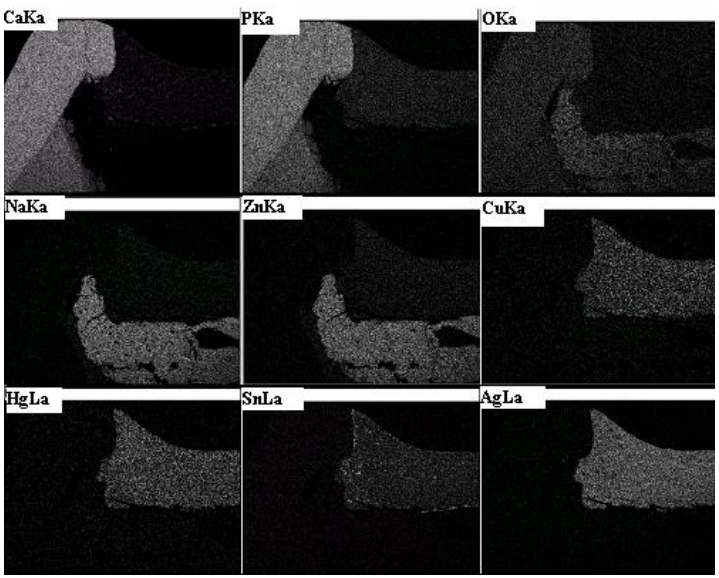
Sample	Beamline	Detection	HgS_{red}	HgO	$HgSO_4$	Corderoite	Reduced χ^2
M1 part. 1	L	Fluorescence		86.4	16.85		0.028
M1 part. 2	L	Fluorescence	26.28		79.95		0.030
M2	A1	Fluorescence	32.85	10.31	19.82	33.47	0.00028
M3	A1	Fluorescence	32.96	10.19	19.79	33.58	0.00030
M4	A1	Fluorescence	33.18	9.91	19.85	33.82	0.00045
M5	A1	Fluorescence	36.78	6.12	18.05	37.28	0.00020

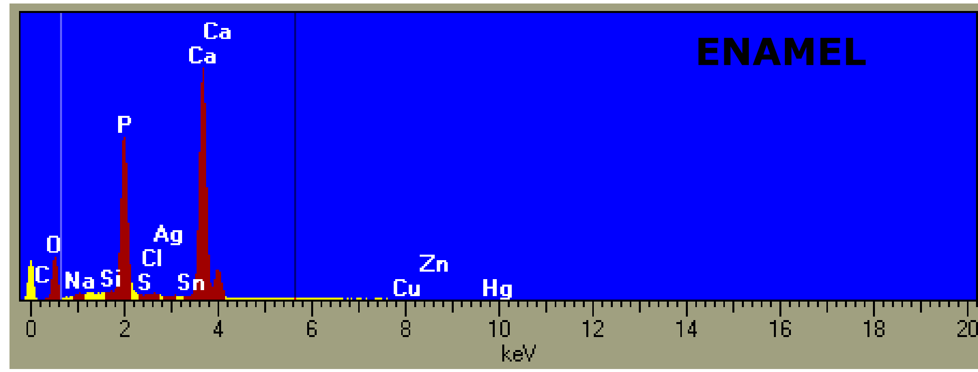
Dental amalgam

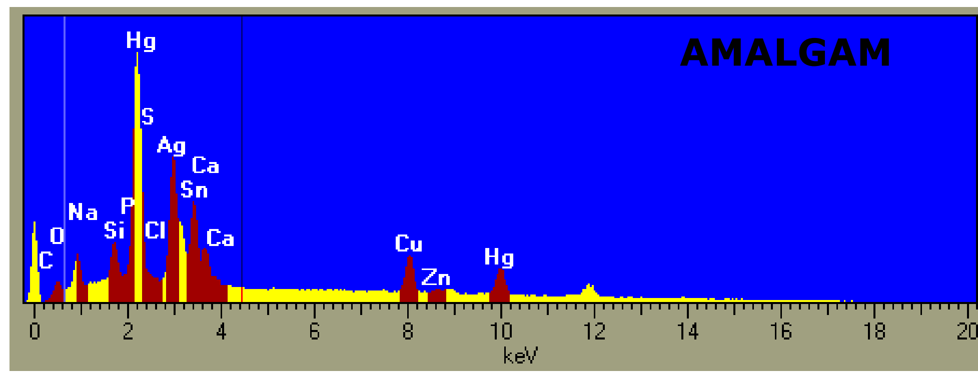
SEM-EDS analysis

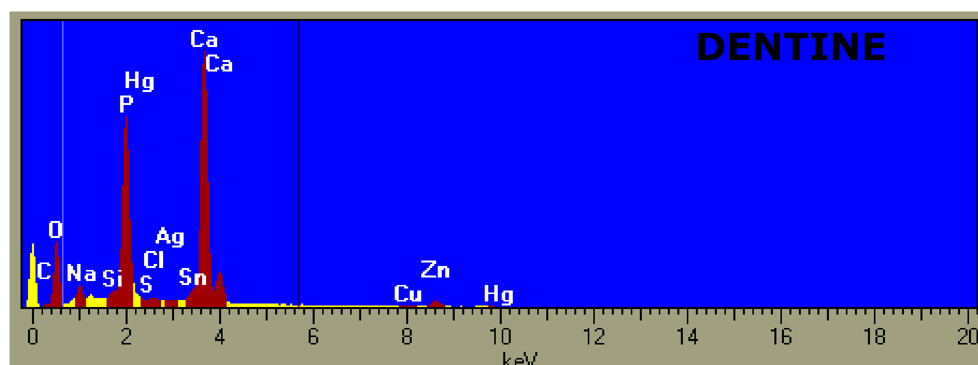
Interface enamel-almalgam-dentine



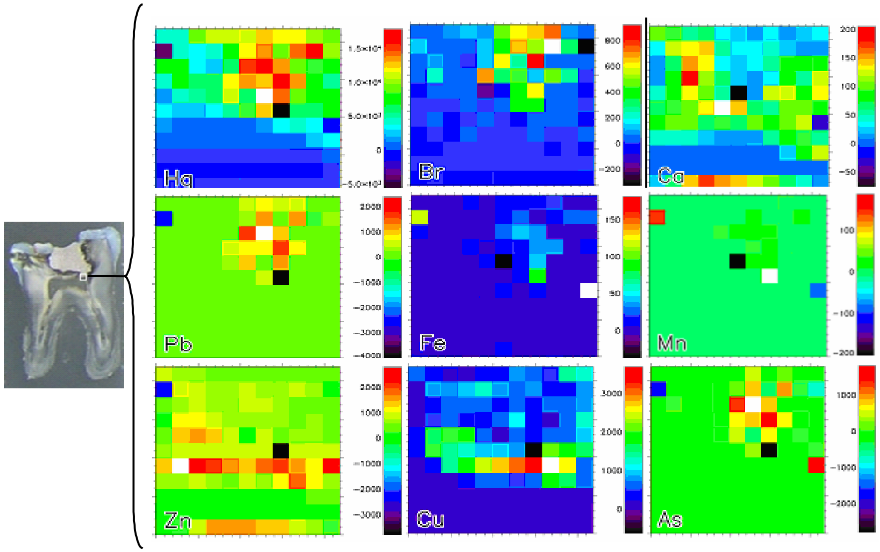








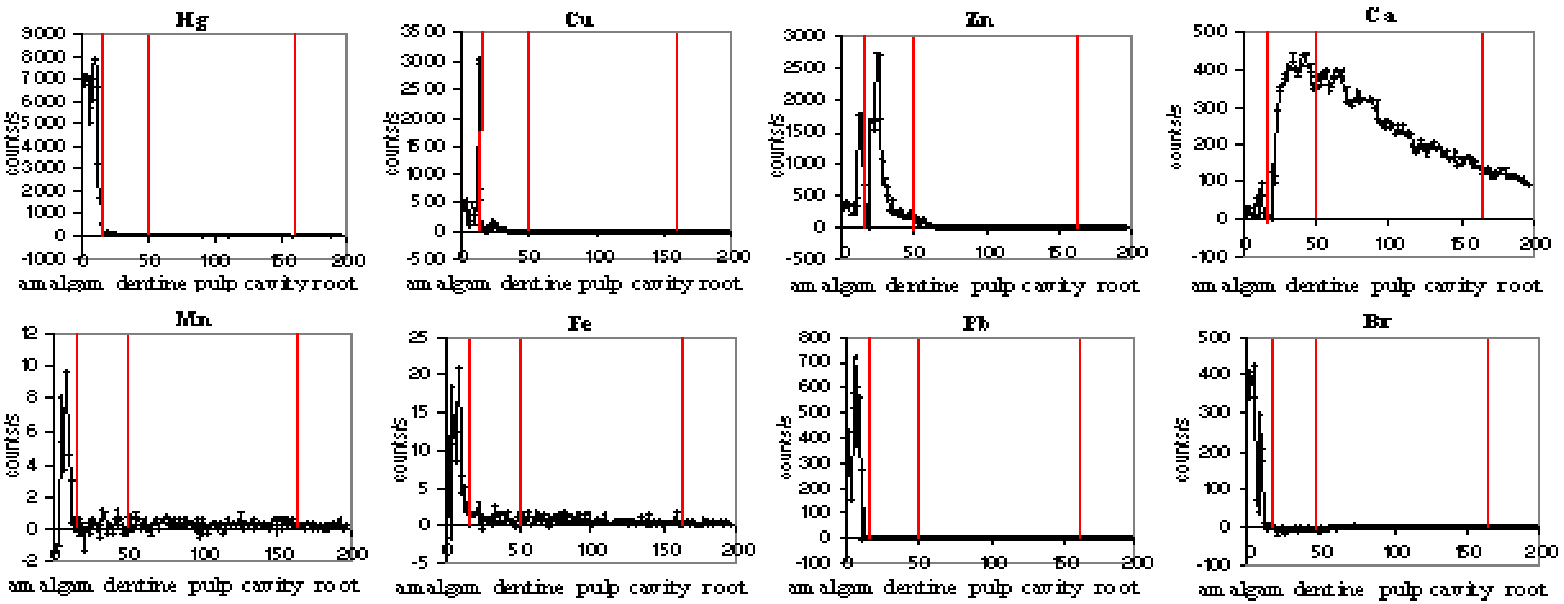
μ-XRF elemental maps and distribution profiles



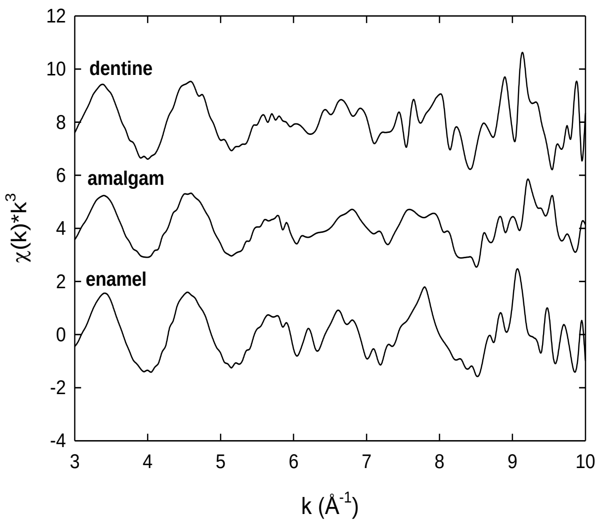
Hg: located in the amalgam region ➡ minimum diffusion

Cu,Zn: higher tendency to diffusion toward the dentine due to a partial exchange with Ca ions

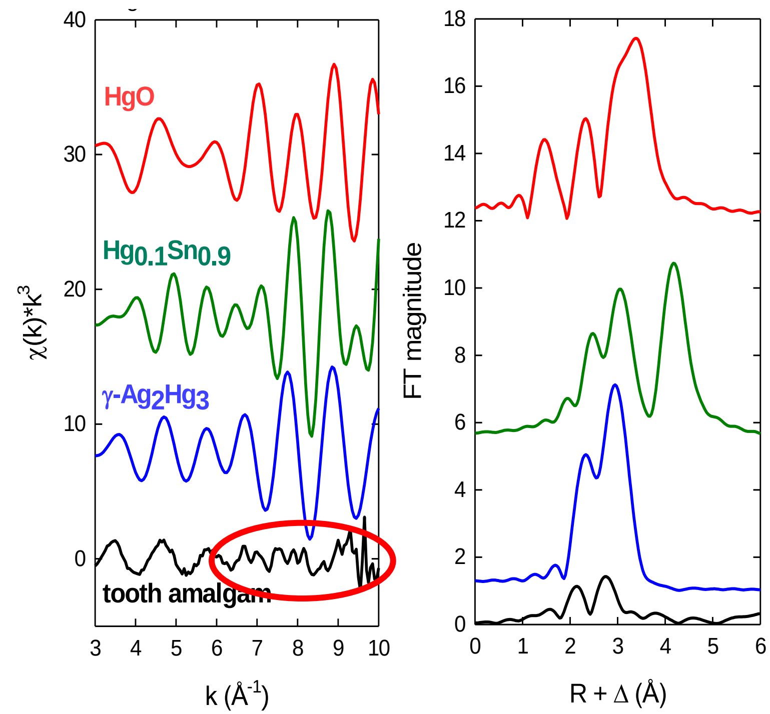
No heavy metals in the pulp cavity and root regions ➡ minimum diffusion to the blood



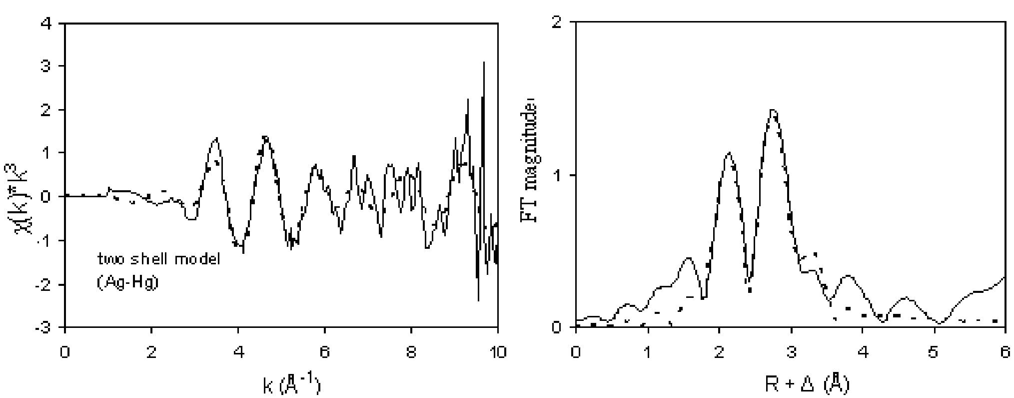
Local environment of Hg by μ-EXAFS



Nearly identical EXAFS features ➡ similar Hg coordination environment



Z	CN	R (Å)	σ^2(Å^2)	ΔE°	red χ^2	S_0^2
Ag	3	2.89	0.02	-1	2.6	0.9
Hg	4	2.97	0.02			



- Presence of the γ-Ag_2Hg_3 phase, which forms during amalgamation
- No O in the first shells ➡ poor (or null) interaction of Hg with the environment
- Large fit values for the Debye-Waller factors ➡ poor data quality at intermediate to higher k values

Conclusions

Conclusions

✓ **XANES and EXAFS spectroscopies** have been shown to be **powerful speciation tools**, with (almost) **no sample pre-treatment**. These techniques have been successfully applied to study both **environmental and biological samples**

✓ **Synchrotron-based microprobe techniques** have been confirmed as a key-tool for the study of **chemical speciation in microscopic environments.** This technique importantly broadens the possibilities for the study of bio/geo/chemical processes taking place at microscopic scale

✓ **Accuracy and reliability of XAS** data may slightly decrease for **complex sample-matrices** (as for environmental samples). The **coupling** with appropriate lab-scale wet techniques (**biosensors, SES, SEM**) is recommended in these cases

✓ Important findings have been driven regarding Hg behaviour in environmental samples. The **presence of 'soluble' salts in Hg-impacted environments** results of an utmost importance and must be taken into consideration in **further risk assessment exercises**

✓ **Stability of mercury in amalgam tooth filling** has been indicated by XAS techniques, although **further diffusion of other heavy metals as Cu and Zn** has been observed

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Thanks to:

Anna Bernaus

Application of X-ray Synchrotron-Based Techniques to the Study of the Speciation of **Hg** in Environmental and Biological Systems

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