X-ray fluorescence analysis

A. Somogyi
ID22, European Synchrotron Radiation Facility, ESRF, Grenoble France

Outline

- What is X-ray fluorescence analysis (XRF)?
- Micro-X-ray fluorescence analysis
- Application of scanning μ-XRF
- X-ray fluorescence tomography and applications
- Combination of μ-XRF with other μ-X-ray techniques (μ-XRD, μ-XANES, μ-tomography)
- Conclusion

Collaborators:

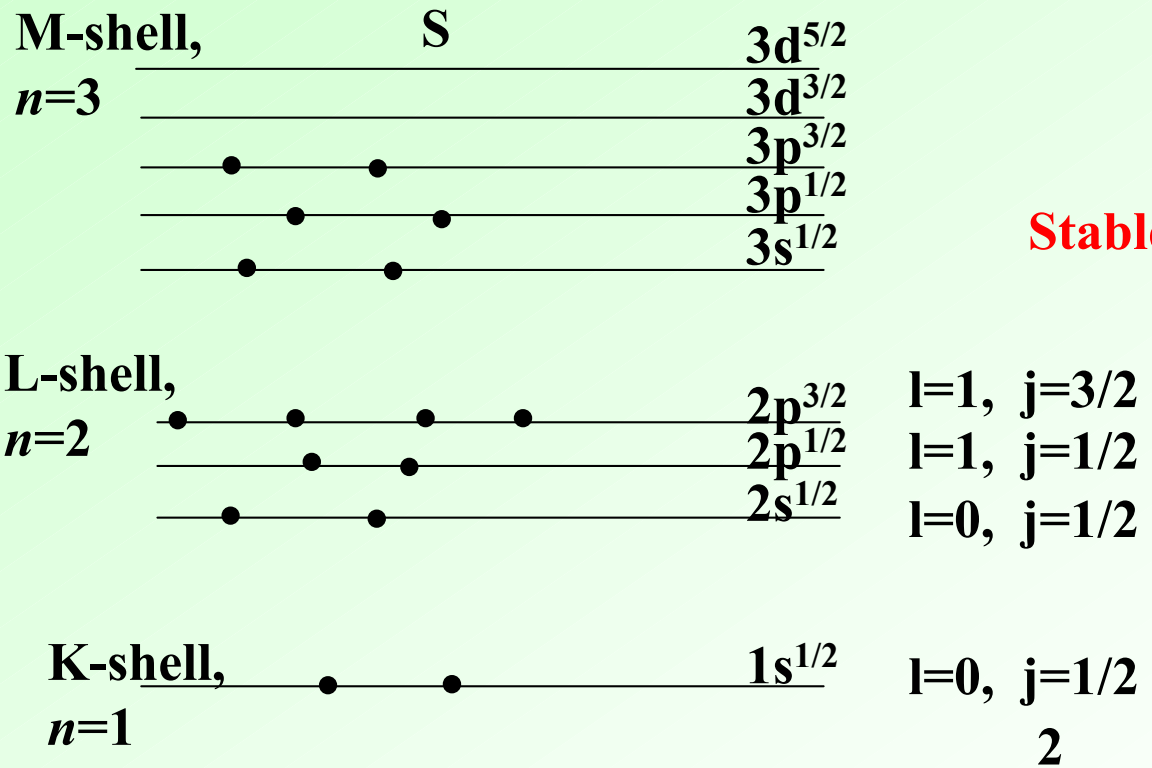
- J. Susini, M. Salome, R. Baker, ID21
- B. Golosio, S. Bohic, M. Drakopoulos, S. Labouré, ID22/ID18F
- R. Toucoulou, ID21/ID22
- B. Fayard, A. Simionovici(CNRS)

What is X-ray fluorescence analysis?

X-ray flurescence spectra:
Originate from a lack of an electron in an inner electron shell

Electron configuration in an atom

- electron states are determined by the *n, l, m, j* quantum numbers
- electron shell: specified by the *n* principal quantum number
- electron subshell: determined by *l, j*
- energy of an atomic electron is determined by Z, *n, l, j*



Pauli exclusion principle

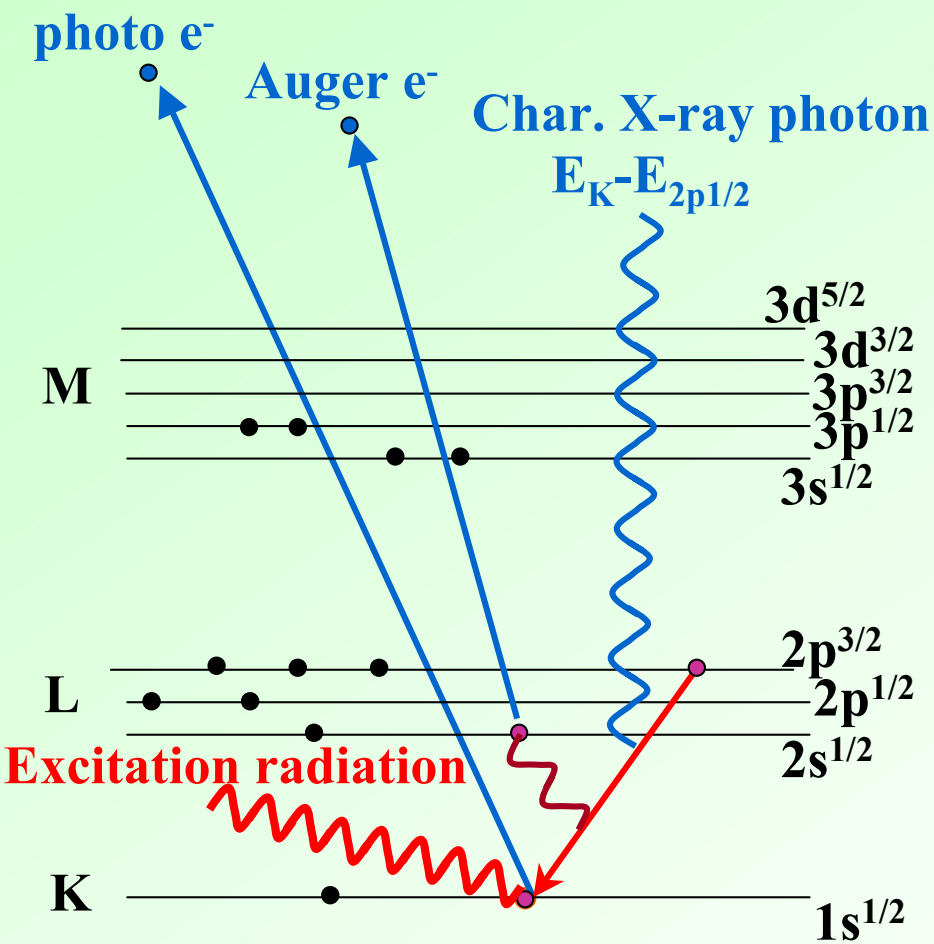
Stable atom: inner electron shells (largest e^- binding energy) are filled

closed subshell: 2j+1 e^-

What is X-ray fluorescence analysis?

Stable state: all the inner shells are filled, till the valance state

Excitation: one electron is removed from one of the inner shells (K, L, …),
'hole' is created by X-ray photons
Electrons
Protons



Deexcitation by readjustment of the electron cloud
electron transition from outer shells

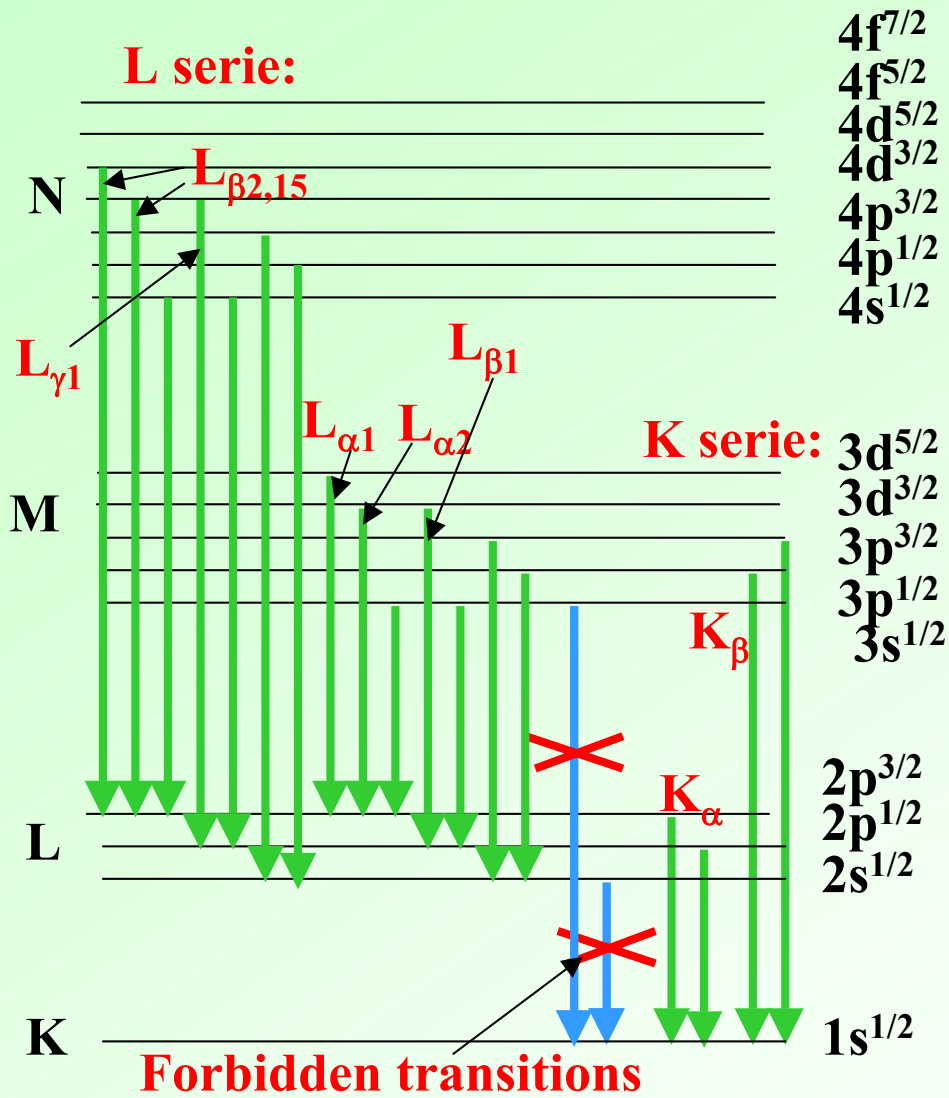
$$E_K > E_L !!$$

E_K-E_L will be released, e.g. by

Characteristic X-ray photon
Photoelectrons
Auger electrons

How does an X-ray spectrum look like?

Diagramm lines



Electric-dipole selection rules

$\Delta n \neq 0$

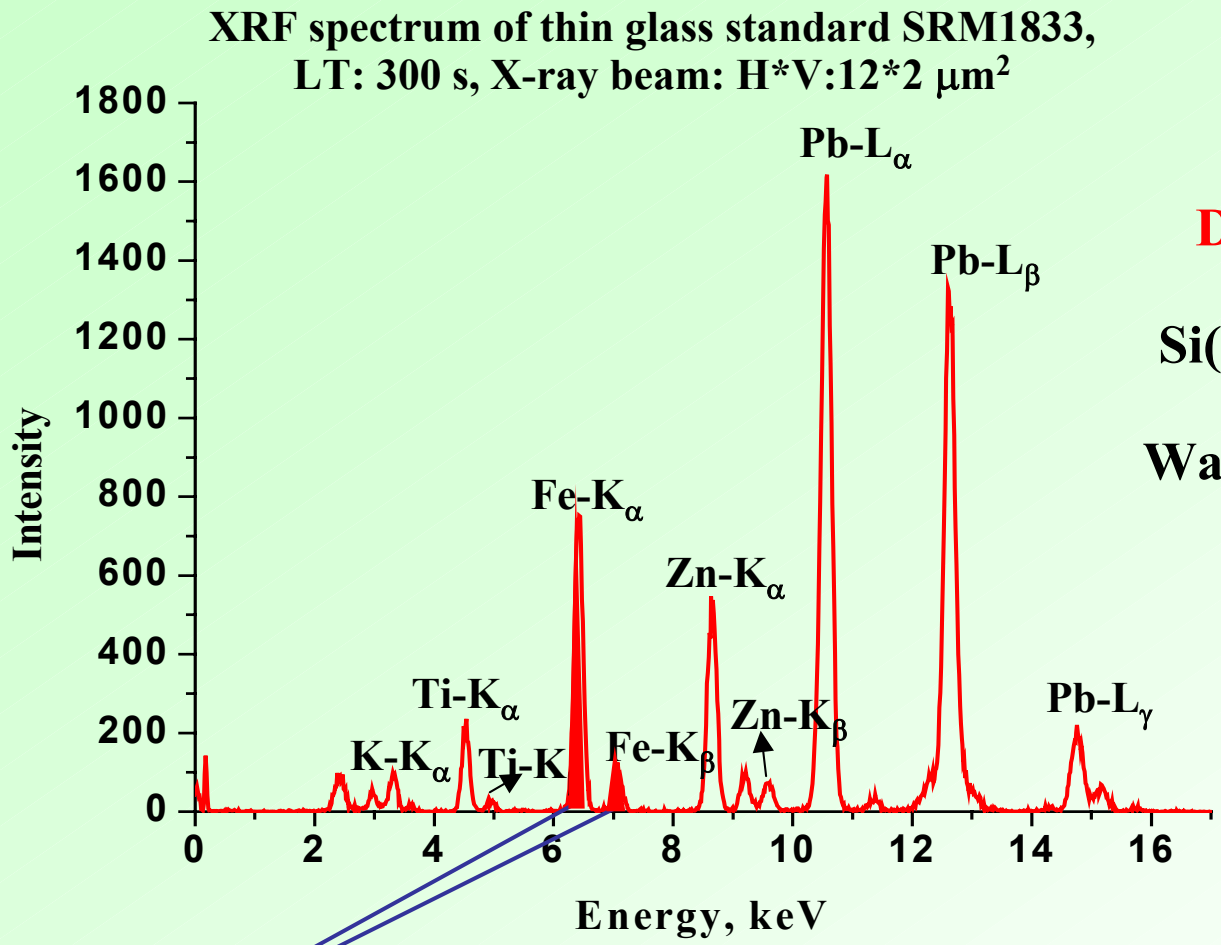
$\Delta l = \pm 1$

$\Delta j = 0, \pm 1$

First 4 elements, H, He, Li, Be have no characteristic X-ray diagramm lines

New transitions become possible with the filling up of the outer electron shells

How does an X-ray spectrum look like?



Detection of XRF spectra:

Si(Li) solid state spectrometer

Wave-length dispersive crystal spectrometer

Energies of the X-ray lines → **qualitative analyzis**

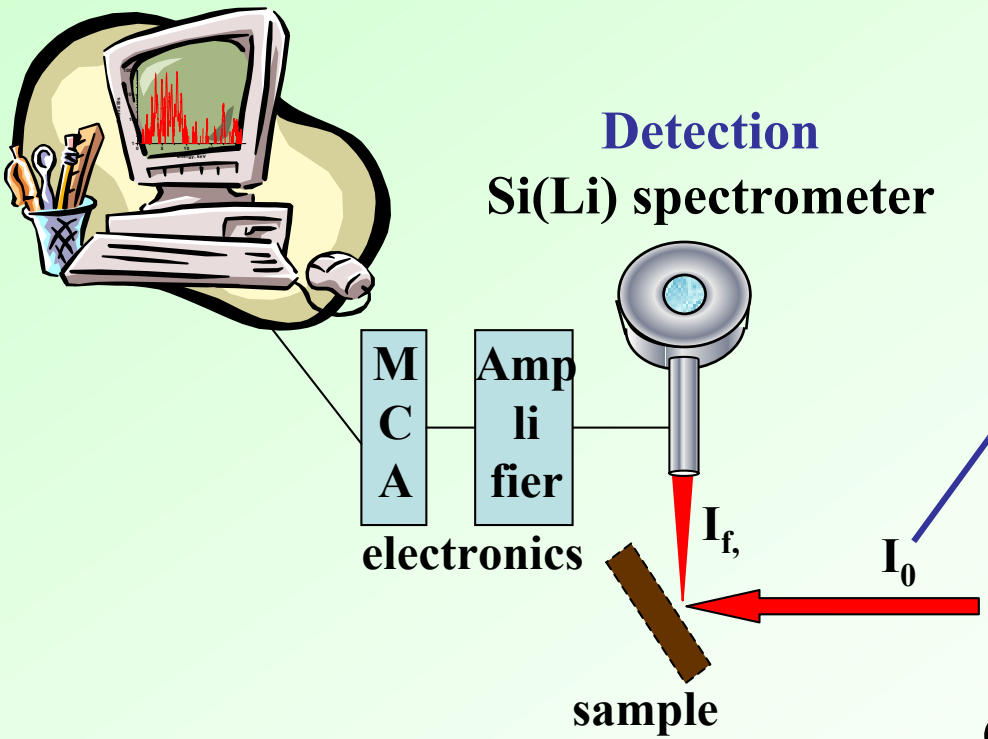
Intensity of a given X-ray line → **~number of a given atom in the excited volume, quantitative analysis**

What is X-ray fluorescence analysis?

How can we knock out an electron from an inner electron shell?

With X-ray, γ-ray, electrons, ions with $E>E_K$ or $E>E_L$

X-ray fluorescence analysis:
Inner e^- shell excitation by X-rays
Detection of characteristic X-ray photons (X-ray spectra)



X-ray excitation sources:

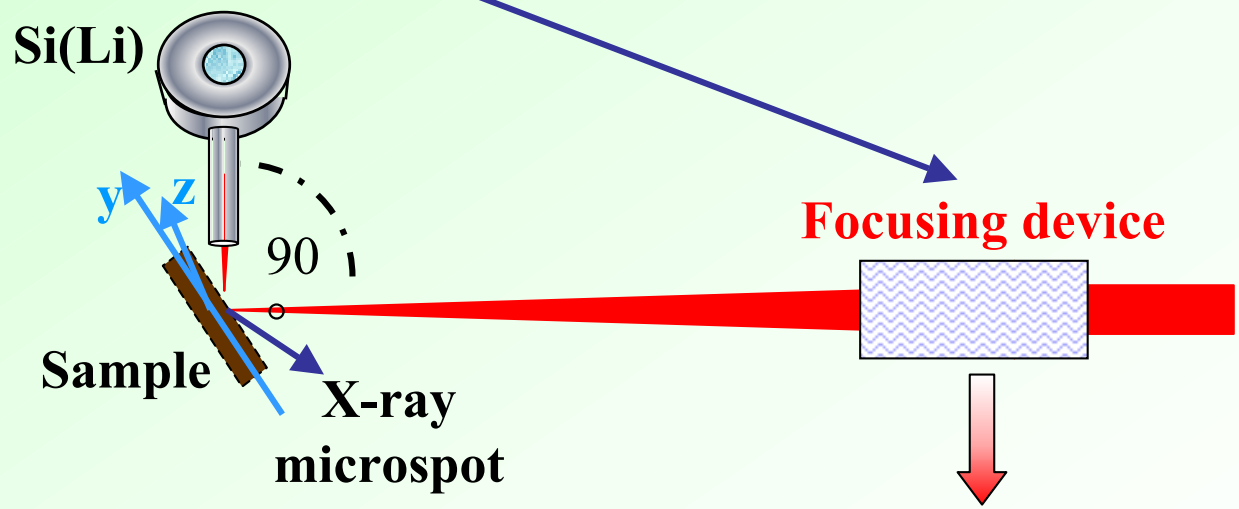
- **X-ray radioisotope**
- **X-ray tube**
- **Synchrotron beam**

Laser like X-ray beam with low divergence and high spectral brilliance

Micro-X-ray fluorescence spectrometry

High efficiency demagnification/collimation of the X-ray source

XRF spectra → elemental composition of the illuminated micro-spot of the sample



Focusing device

Sample can be raster-scanned in the μ-beam

Scanning μ-XRF

Spatially resolved 2D elemental composition

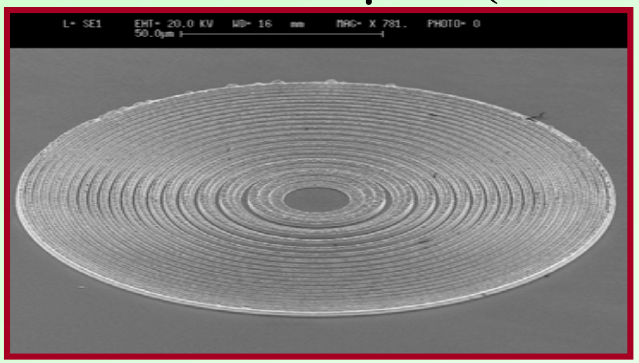
KB mirror
Compound Refractive Lens (CRL)
Fresnel Zone Plate (FZP)
Capillary
Slits/pinhole

Micro-X-ray fluorescence spectrometry
Focusing devices

Fresnel Zone Plates (FZP)

Diffractive Optics

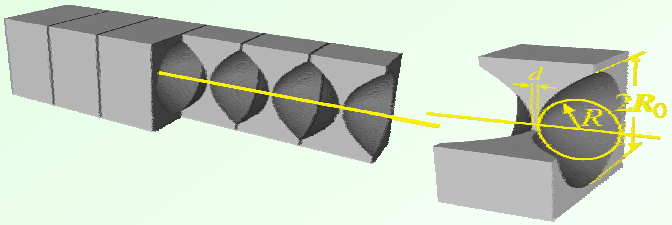
- diffraction gratings of increasing linear density
- 50-60 % efficiency
- spot size:< 0.1 x 0.1µm^2 (for low E)

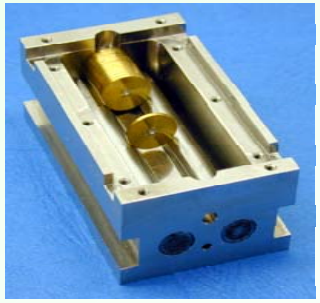


Compound Refractive Lenses (CRL)

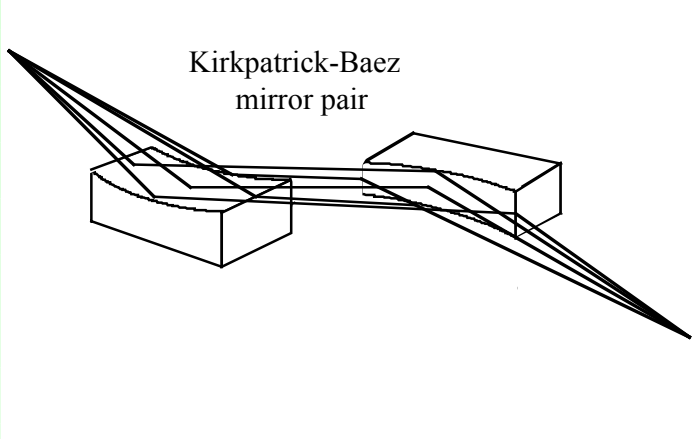
Refractive Optics

- parabolic lenses - reduced aberrations
- variable n assemblies: tune f and L_2
- high yield for high E
- spot size: ~2 x 12 µm^2





Bent mirrors Kirkpatrick-Baez, (KB mirror pair)



Reflective optics

- 60-70 % efficiency
- acchromaticity
- Multilayer mirror for high energy
- spot size: ~1 x 3 µm^2

Synchrotron radiation induced scanning μ-XRF

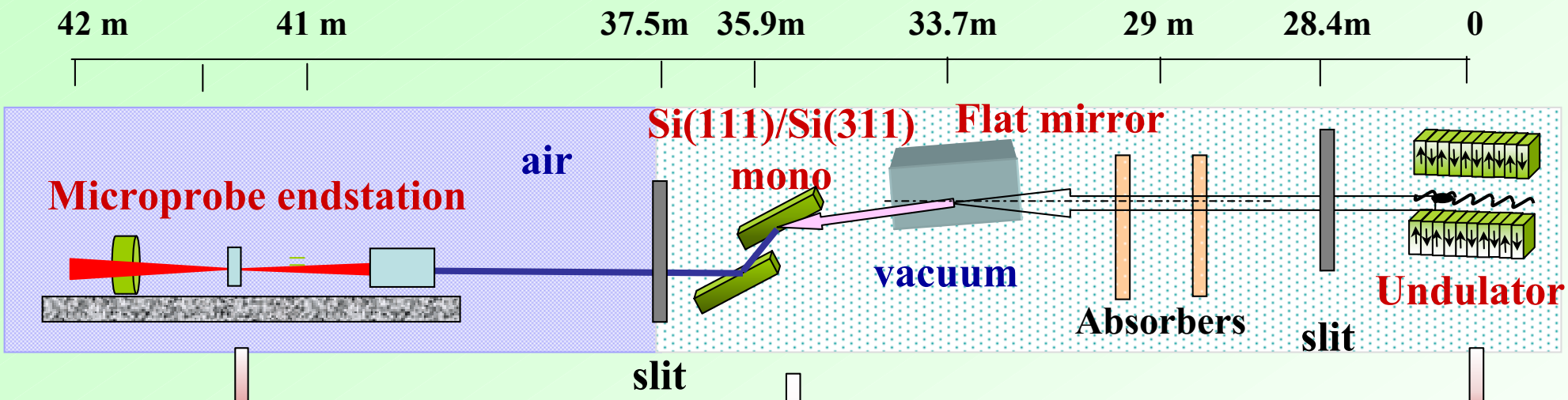
ID21, ID22 beam-lines of the European Synchrotron Radiation Facility (ESRF)

	ID21 X-Ray Microscopy	ID22/ID18F Micro-XRF,Imaging, Diffraction
•Energy range:	2-8 keV	6-70 keV
•Spatial resolution:	0.1 - 1.0 μm	1.5 - 3.0 μ m
•Monochromator:	Si 111 or Si 220	Si 111 or Si 311
•Detection:	parallel multiple detection	
•Fluorescence:	HPGe	Si(Li)
•Transmission:	photodiode	photodiode, ion. chamber
	operation in air/vacuum	operation in air
•Detectable elements:	Z<26 (Fe) K-lines	14<Z<72 (Hf) K-lines
(by XRF)	Z<64 (Gd) L-lines	72<Z L-lines

Applications:

Geochemistry, Biology, Environmental Sciences, Materials Science…

Schematic layout of the ID22 beam line and the microprobe end-station

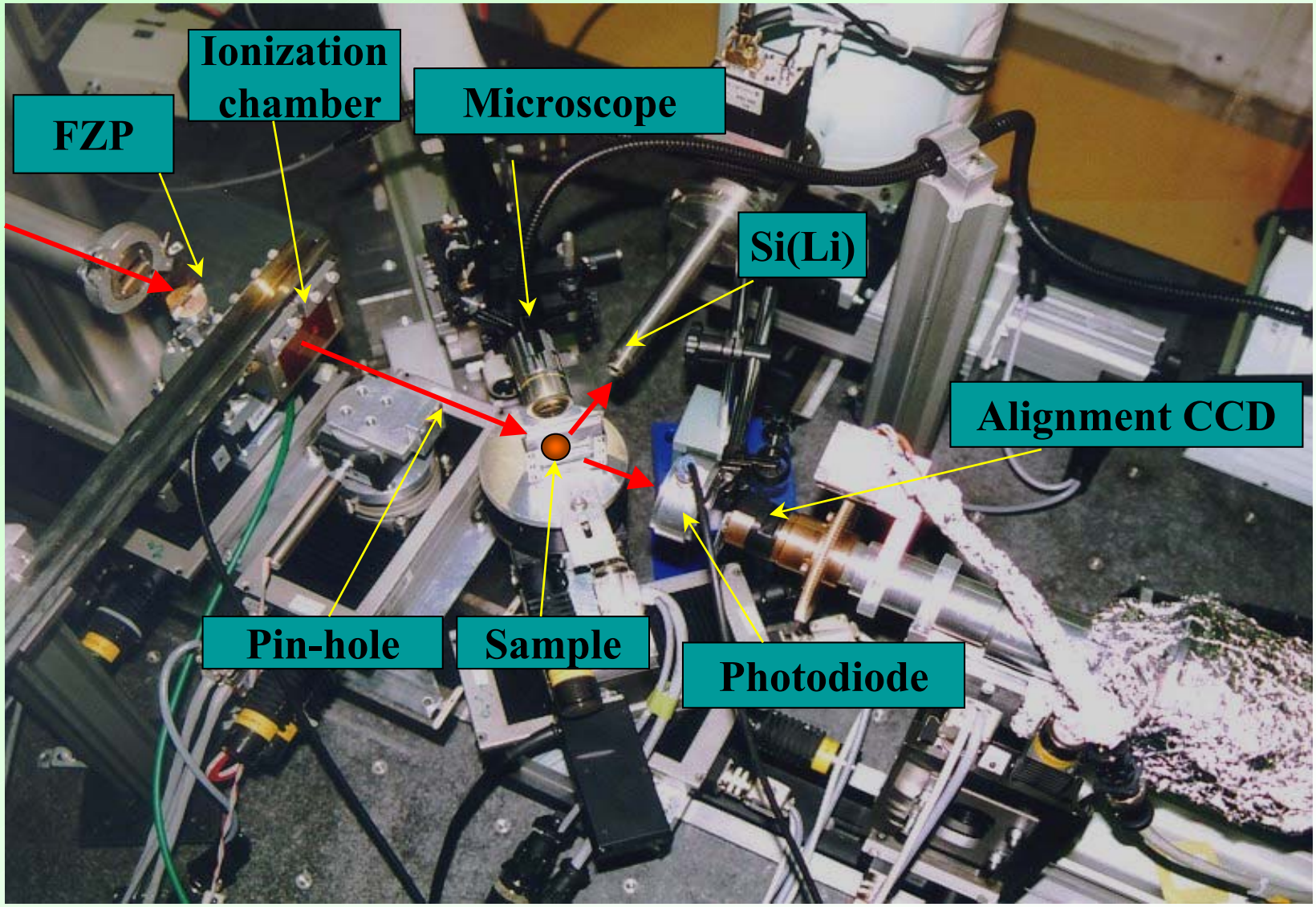


Focused micro-beam,
Spot-size (H×V): 3 × 1.5 μm²
Flux: 10^{10} - 10^{11} ph/s

High beta section
Source size (H×V): 700 × 30 μm²
Div. (H×V): 30 × 20 μrad²

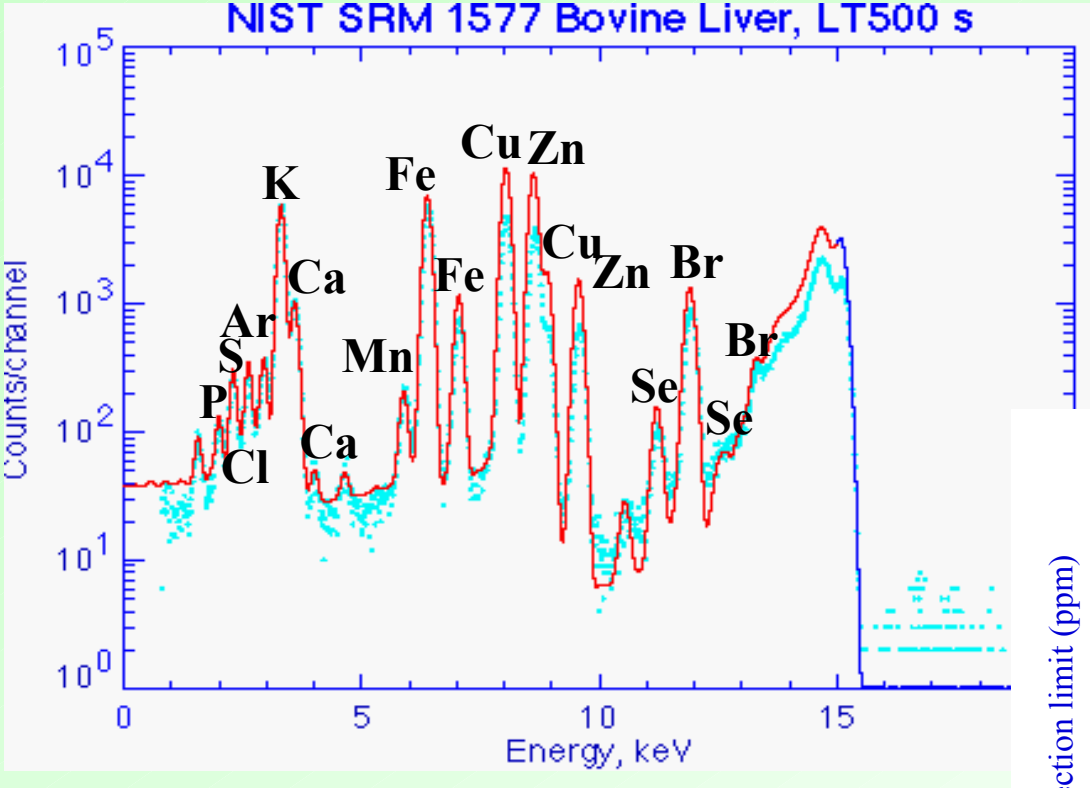
Tunable, monochromatic X-ray beam
E range: 6-70 keV
E resolution: $\Delta E/E \approx 10^{-4}$
or
Mirror reflected pink beam: one full undulator harmonics

X-ray microprobe set-up at ID22



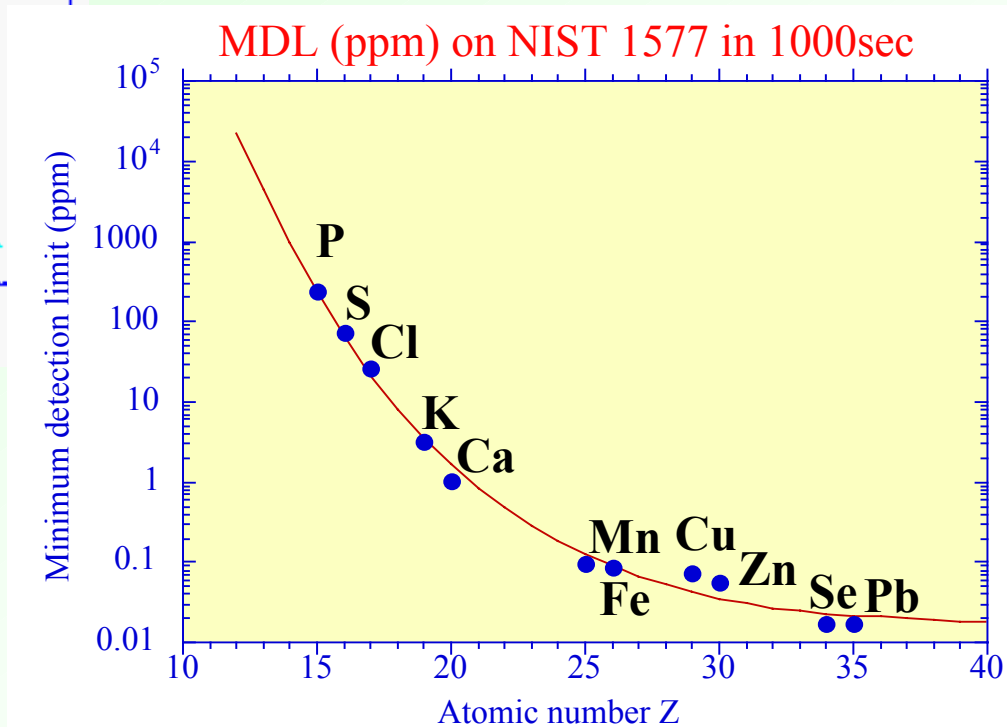
X-ray microprobe set-up at ID22, ESRF

Minimum limit of detection



Detection limit/1000 s:
≈20 ppb
≈0.4 fg

E=15 keV, 1 x 5 μm²



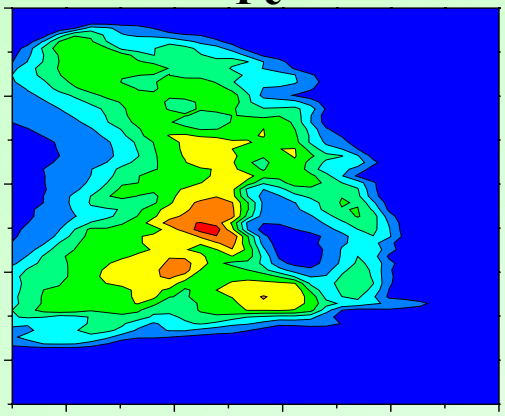
10^{10}-10^{11} photons/s in the focused beam

Scanning micro-XRF, geological applications
Inclusions in obsidian

In collaboration: A.Z. Kiss, IBA-ATOMKI, Gy. Szoor, Univ. of Debrecen, Hungary

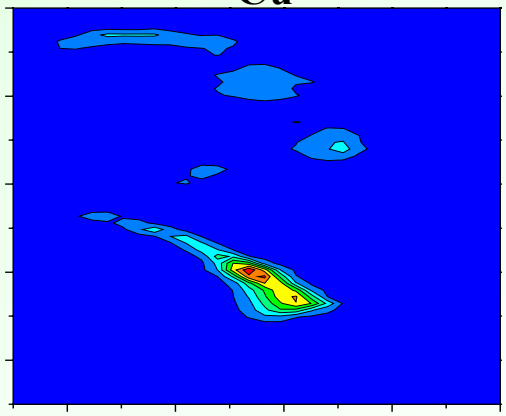
Flat obsidian slice of ~50 μm thickness, LT:6 s/pixel, spot: H*V=8*1.5 μm^2, ID22 Vinicky, Slovakia

Fe

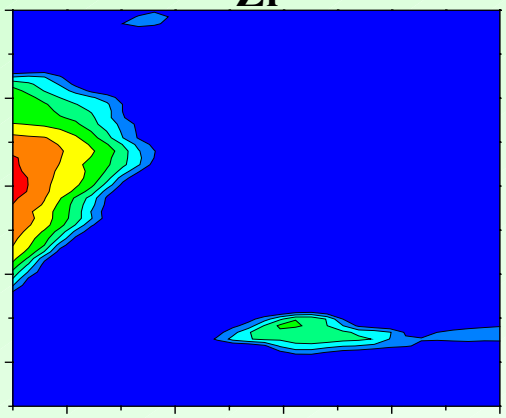


Obsidian: volcanic glass, inclusions: mineral phase of μm size. Its chemical composition is characteristic to the geographical source.
⇒Distinction of ancient archeological obsidian sources from e.g Hf/Zr, Y/Sr conc. ratio.

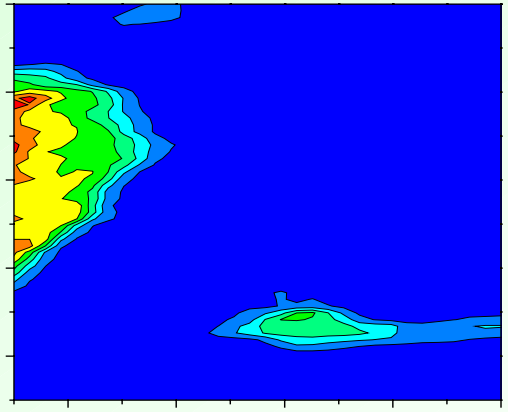
Cu



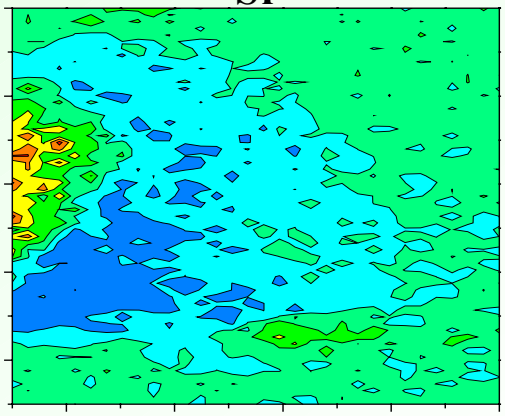
Zr



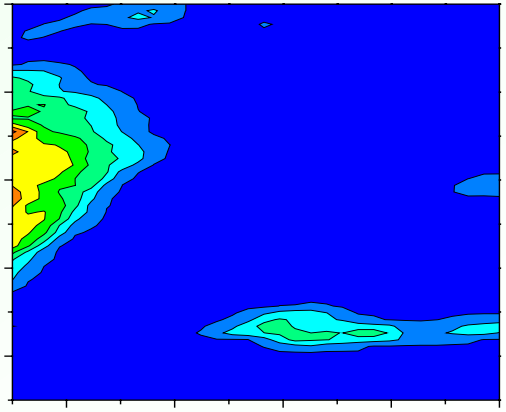
Hf



Sr



Y



Combination with other analytical techniques, LA-ICP-MS, SEM-EDAX, PIGE, PIXE, optical microscopy

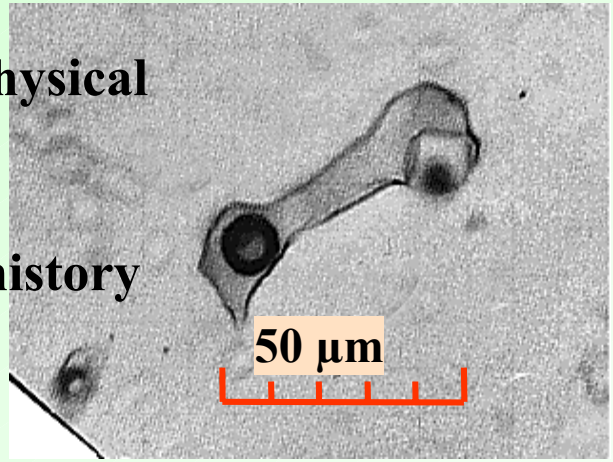
Scanning micro-XRF, geological applications

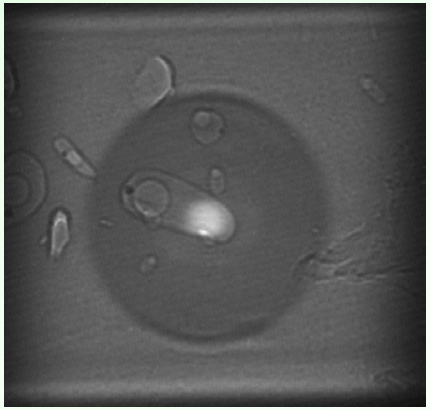
Quantitative mapping of trace elements in fluid inclusions

P. Philippot, B. Ménez, Univ. Paris VI, France, A. Simionovici, CNRS, Lyon

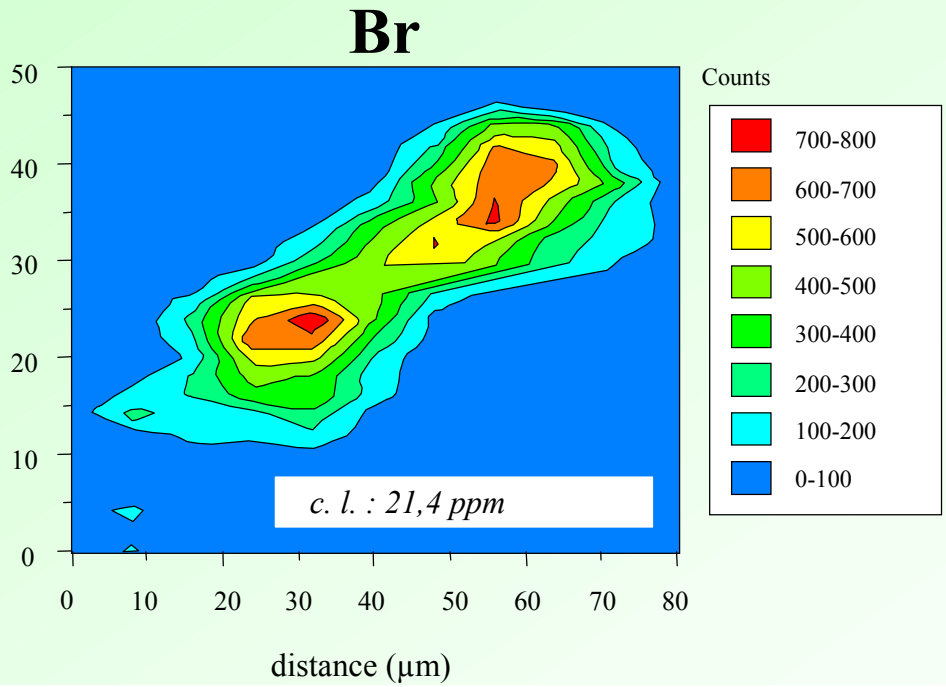
Fluid inclusion: preservation of chemical, physical porpeties of the original parent fluid (if closed system)

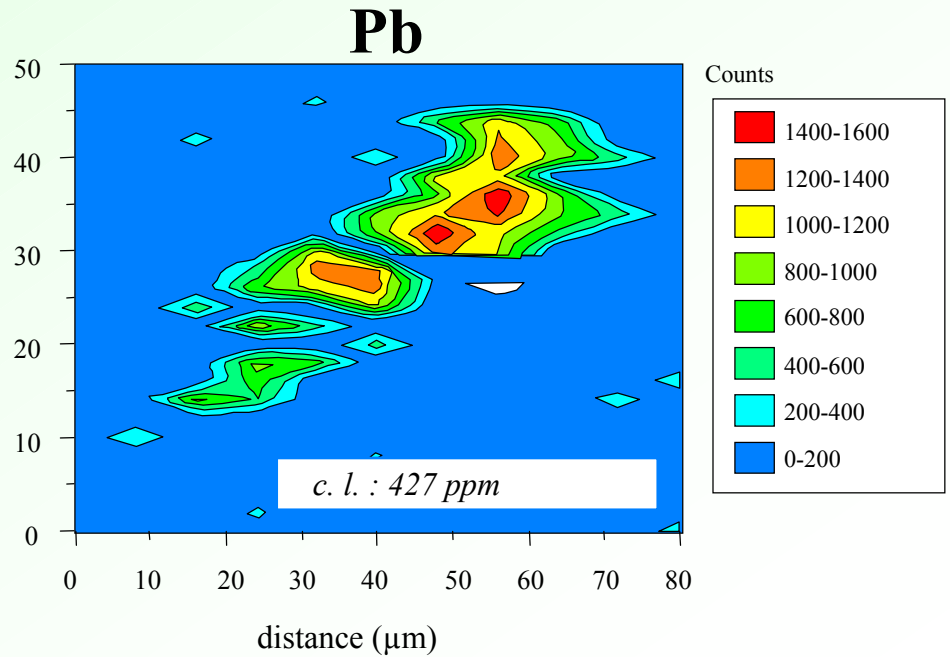
Unique direct fossil samples of the Earth's history





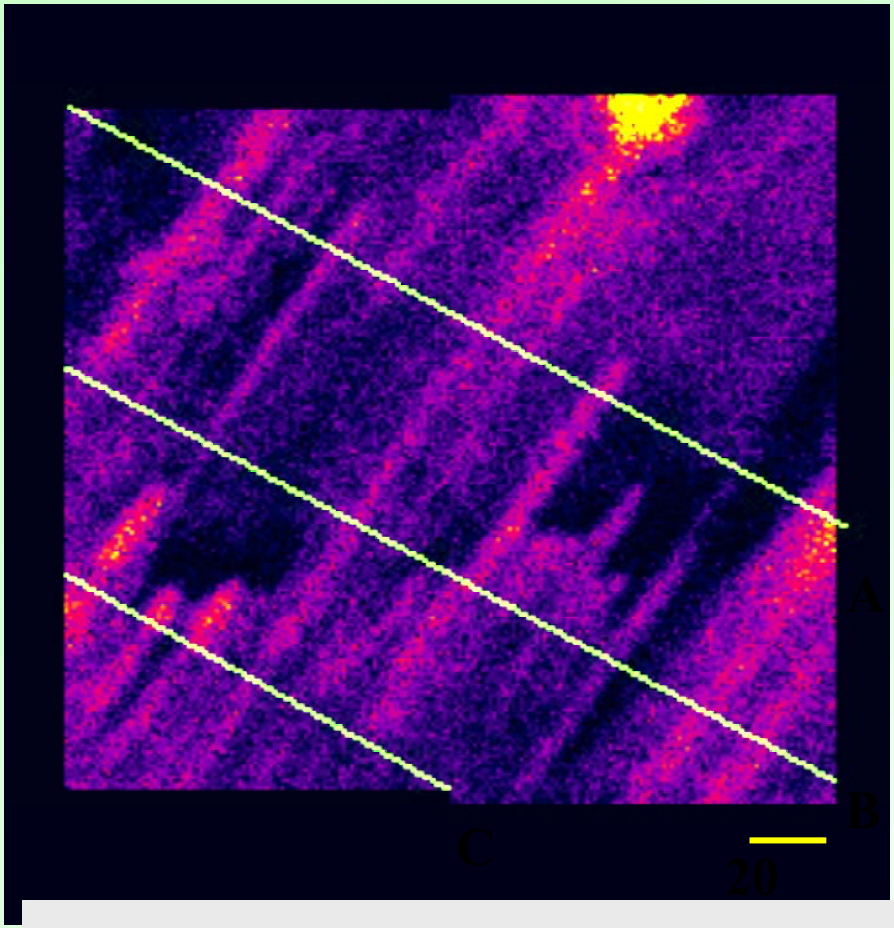
E=12 and 20 keV, (FZP+CRL) focusing non-destructive analysis, t ≈ 5 - 30 s/pt





Scanning micro-XRF, geological applications

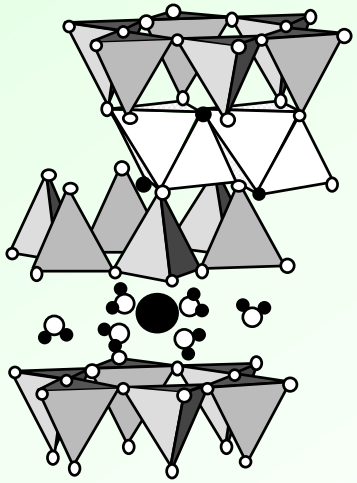
Oriented Meso-structures in clay gels, ID21



- Wyoming montmorillonite gel (50g/l), Prepared as hydrated sample (in vacuum)

- Excitation energy 2.5 keV
- Fluorescence yield of Silicon

- Spatial resolution < 1 μm^2



○ Oxygen

● Hydroxyl

Water molecules

● Exchangeable cation

$(Si_{7.73}Al_{0.27})\ (Al_{3.06}Mg_{0.46}Fe^{II}_{0.03}Fe^{III}_{0.44})\ Na_{0.76}$

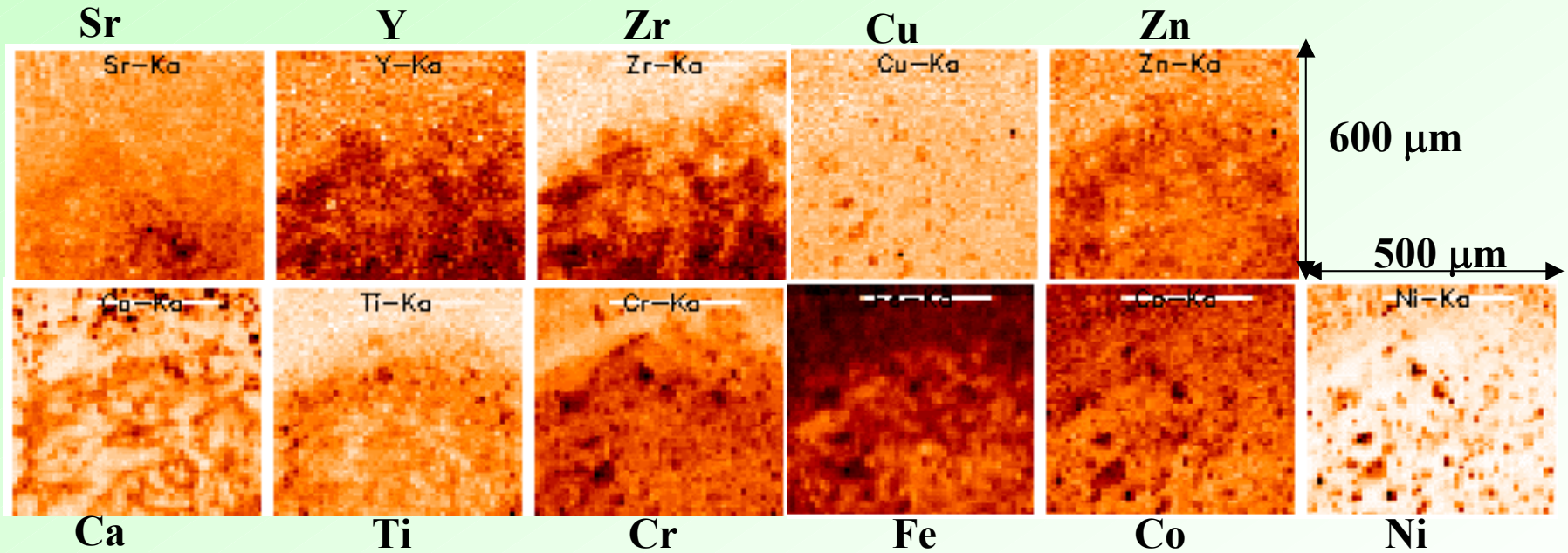
Observation of periodical ordering on length-scales <u>2 orders of magnitude</u> larger than expected/known before

(I. Bihannic et al., Langmuir, 17(14) (2001)

Scanning micro-XRF, astrochemical applications
Allende meteorite

In collaboration with F. Adams, K. Janssens, B. Vekemans, L. Vincze Univ. of Antwerp,Belgium

Mapping one part of a chondrule: 50(10 μm)x60(10 μm), LT/pixel: 10 s, ID18F



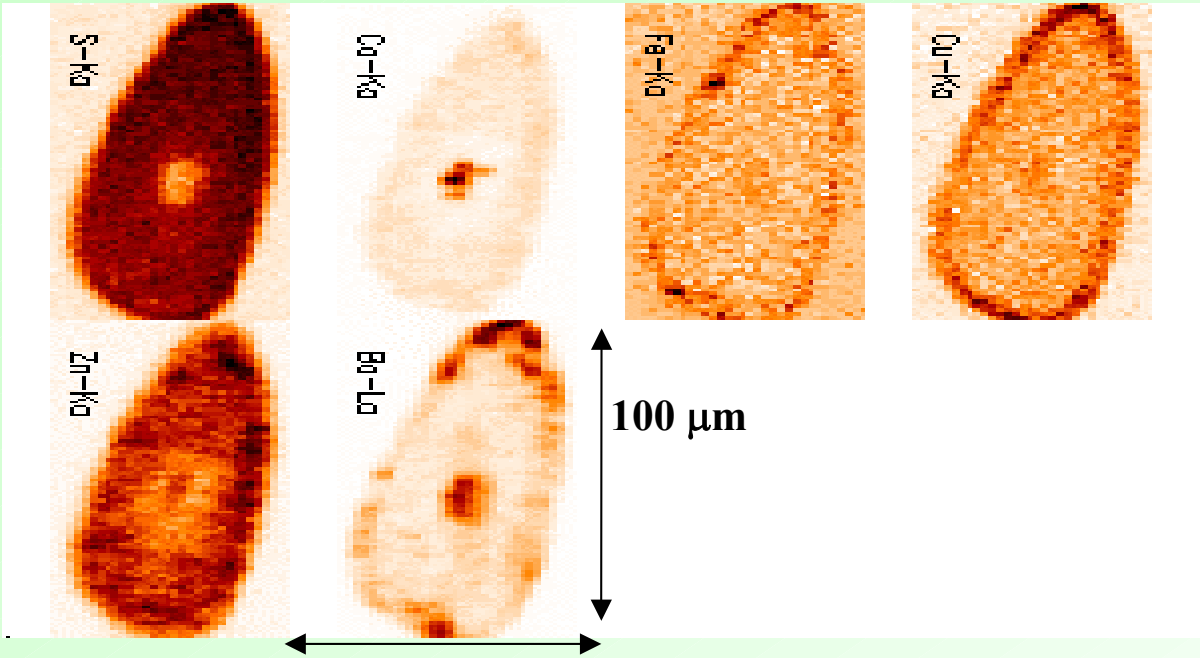
Meteorites are the only objects from the early stage of the solar system available for research, carbonaceous chondrites are one of the oldest objects of the solar system.

correlations between different elements,

possible formation mechanism of chondrule on the basis of Zn distribution?

Scanning micro-XRF, biological applications
XRF mapping of hair sections, ID18F

In collaboration with S. Bohic, ID22, ESRF, France, Y. Duvault: L'Oréal, P. Dumas: LURE, France



Aim of the study:

Anomalies of elemental distribution: stress? Chemicals?

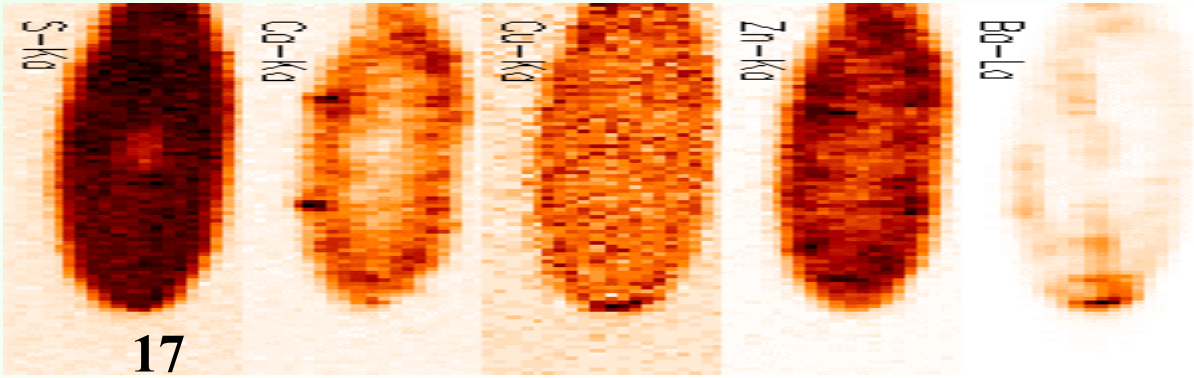
Effect of cosmetics, new developments

Medical diagnostics?

10 µm thick hair sections, E: 17 keV, spot size 2x4 µm^2, LT:7 s/pixel

Needed:

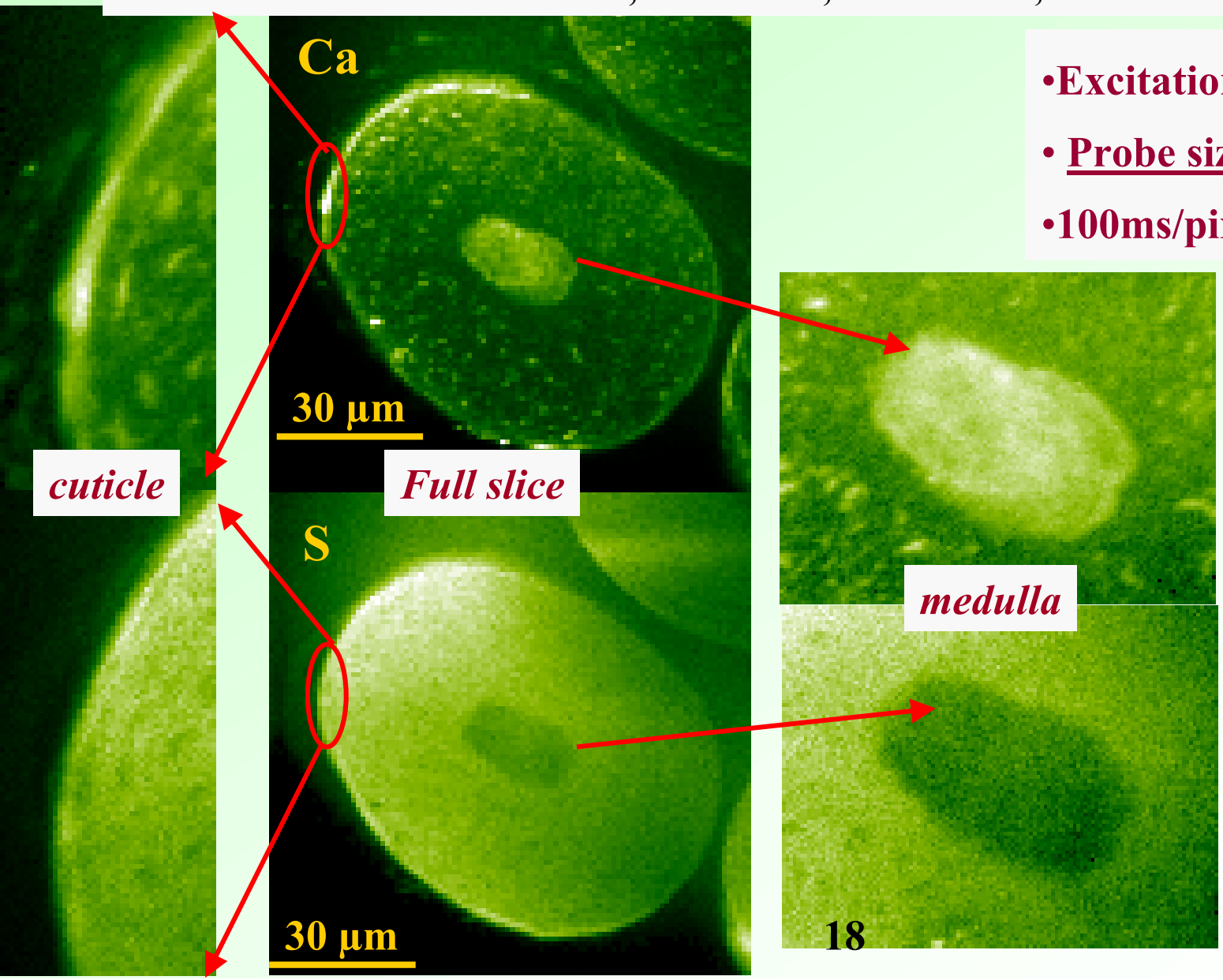
Large number of samples !!!
Complementary techniques, SAX, IR
Careful sample preparation

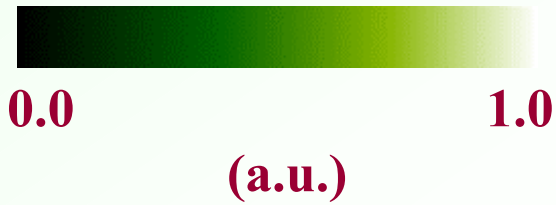


XRF mapping of hair sections, ID21

C. Mérigoux, F. Briki, L. Kreplak, J. Doucet, LURE, Orsay.
J. Susini, M. Salomé, ESRF-ID21, Grenoble.

- Excitation Energy: 4.1keV
- Probe size: 0.20x0.24µm^2
- 100ms/pixel





Scanning micro-XRF, biological applications
Single cell spectroscopy

S. Bohic, A. Simionovici, ESRF, Ortega R - Devès G. , CNRS, Bordeaux CNRS Bordeaux, Medical beamline, IBS, CHU-G

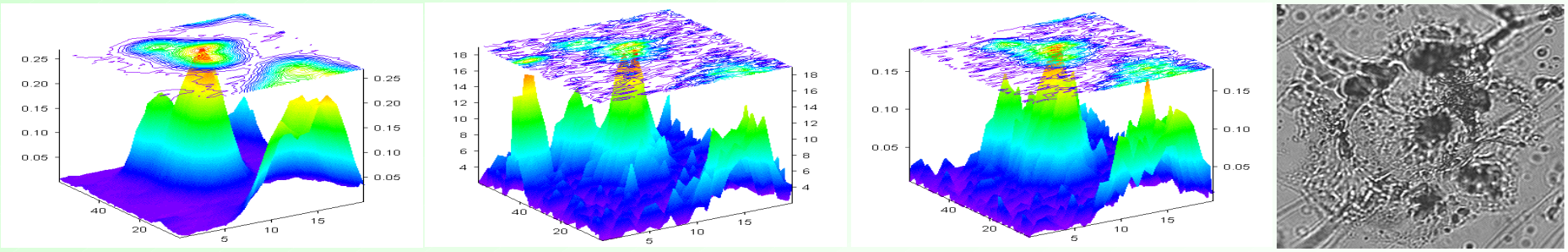
Aim: study of the **anticancer drugs:**

- **biological effects**
- **intracellular distribution**
- **anticancer action**

low 1 mg/ml conc.

of various high Z labelled anticancer drugs used at pharmacological doses

Ovarian cancer cell



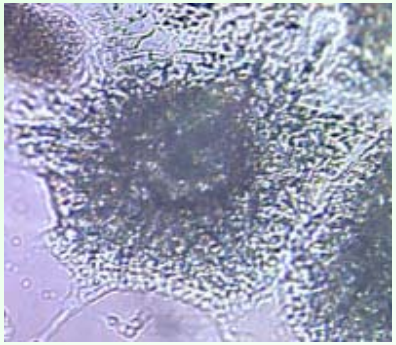
K K_α **Fe K_α** **I L_β** **optical img**

PINK beam: 1 x 5 µm (min), flux ≥ $5 \cdot 10^{11}$ ph/s , CRL lenses
Non-destructive: dry or freeze-dry samples, t ≤ 5 µm
Mapping: 2-4 hours, 1-2 sec./point (PINK),
t > 20h (monochromatic)

Scanning micro-XRF, biological applications

Intracellular distribution of $GaNO_3$

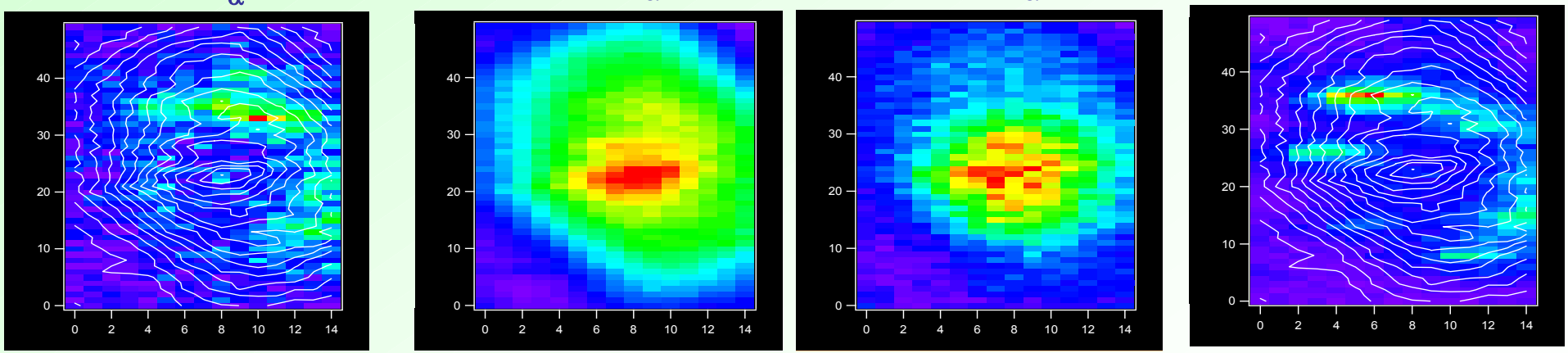
Ortega R - Devès G. , CNRS, Bordeaux ---- ID22: S. Bohic, A Simionovici



- 250 mM Gallium nitrate – 48 H , ⇔ 50% inhibition growth
- Cells grown as monolayer- cryofixed & lyophilized.
- E =14 KeV, beam size 2x10 μm^2, Flux=2.10^{10}ph/s, in air
- Al-Compound Refractive lenses (CRL)
- Dim. 50x60 μm^2, 5 sec/points, pixel 1x4 μm^2

Ga : average of 40µg/g dry mass

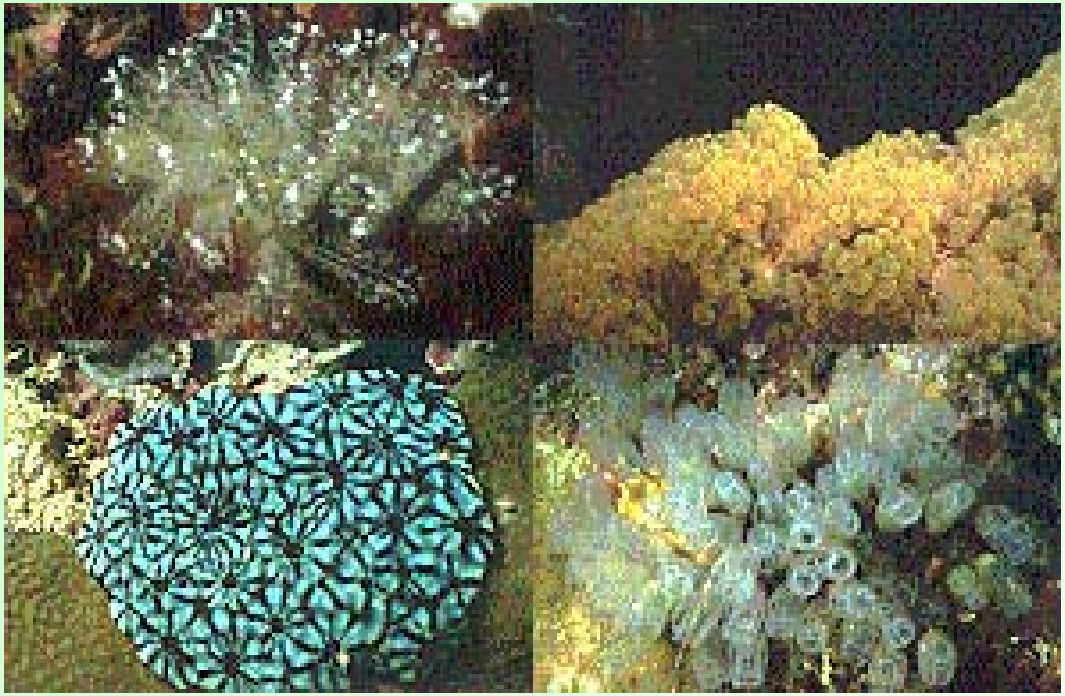
Fe-K_α K-K_α Zn-K_α Ga-K_α

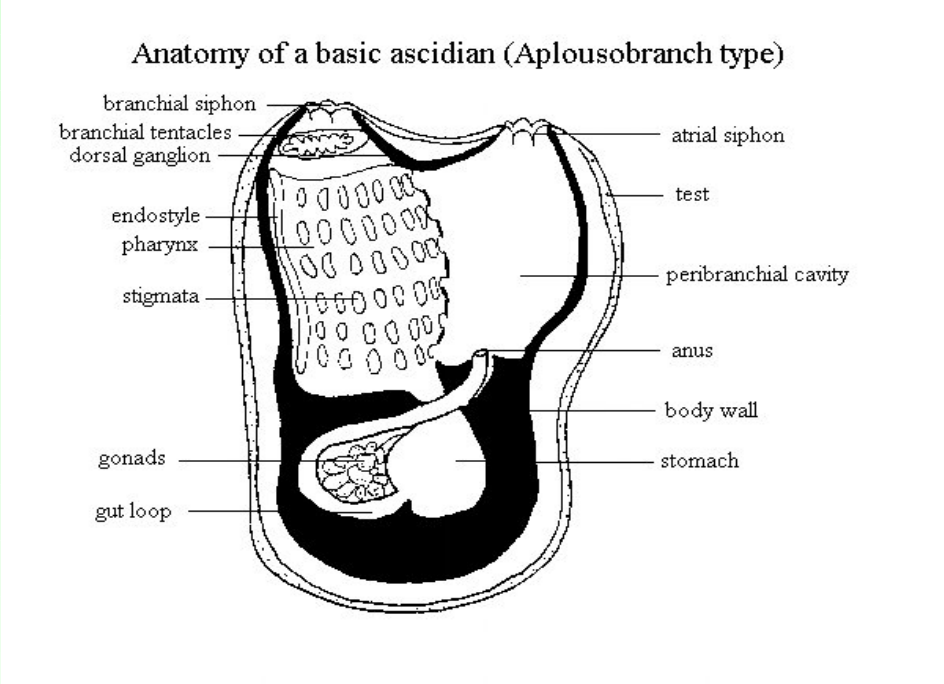


- Localisation of the gallium in small round structures in the perinuclear region - typical of lysosomial material

Scanning micro-XRF, biological applications

Vanadium accumulation in Ascidians (sea squirts or tunicates)





M. Henze, Z. Physiol Chem, 72, 1911
H. Michibata *et al.*, "Vanadium in the environment, Part 1", 1998

Averaged Vanadium concentration:

Sea water:	**~ 3.5 10^{-8} mol/dm^3**
***Ascidian Gemmata*:**	**~ 3.7 10^{-1} mol/dm^3**
***Ascidian Syndneisis* :**	**~ 1.3 10^{-2} mol/dm^3**

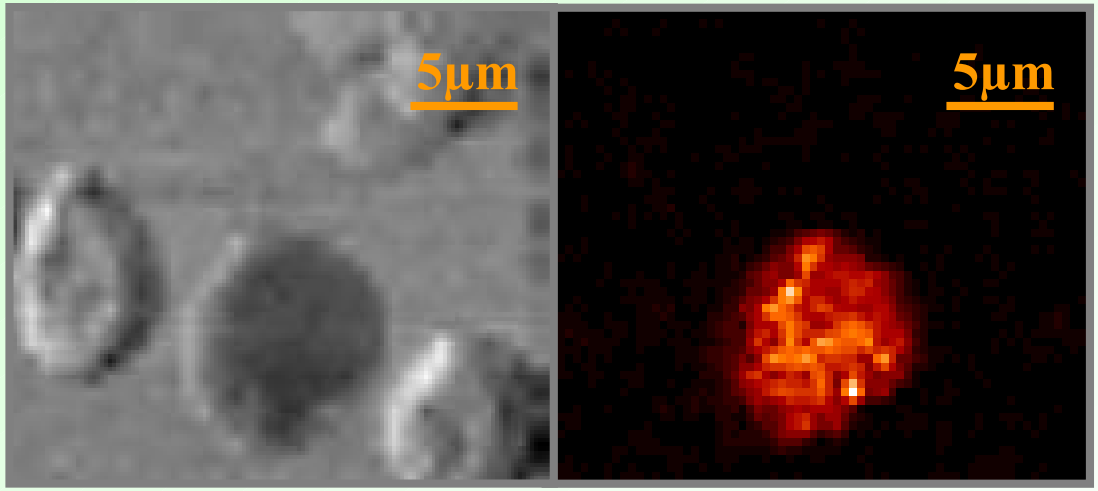
Vanadium accumulation in Ascidians (sea squirts or tunicates)

DIC+Fluorescence on living cells: identification of true vanadocytes, ID21

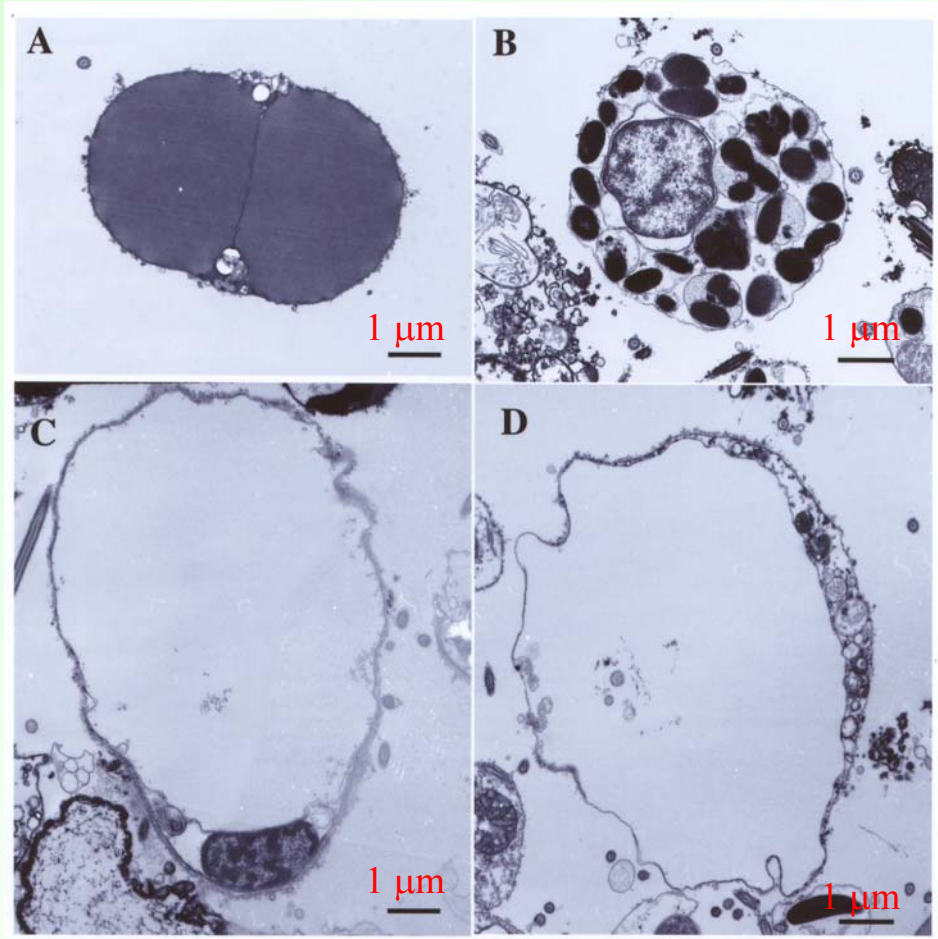
- ✓ 9 to 11 different types of blood cells.
- ✓ Identification of true vanadocytes is still a subject of controversy.

- ✓ Excitation energy: 5.5 keV
- ✓ Probe size: 0.3x0.3µm2
- ✓ Dwell time: 0.1 s/pixel

Vanadium< 300ppm



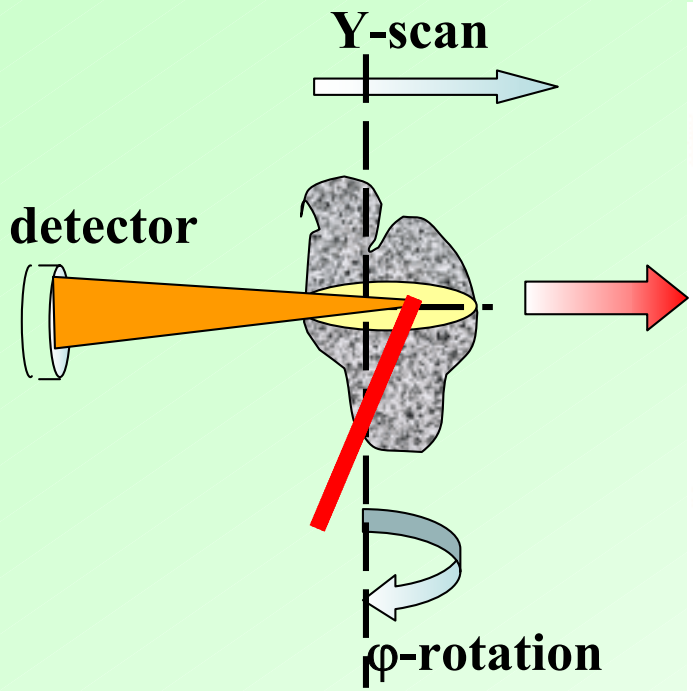
T. Ueki *et al. Zoological Science*, 19, (2002) 22



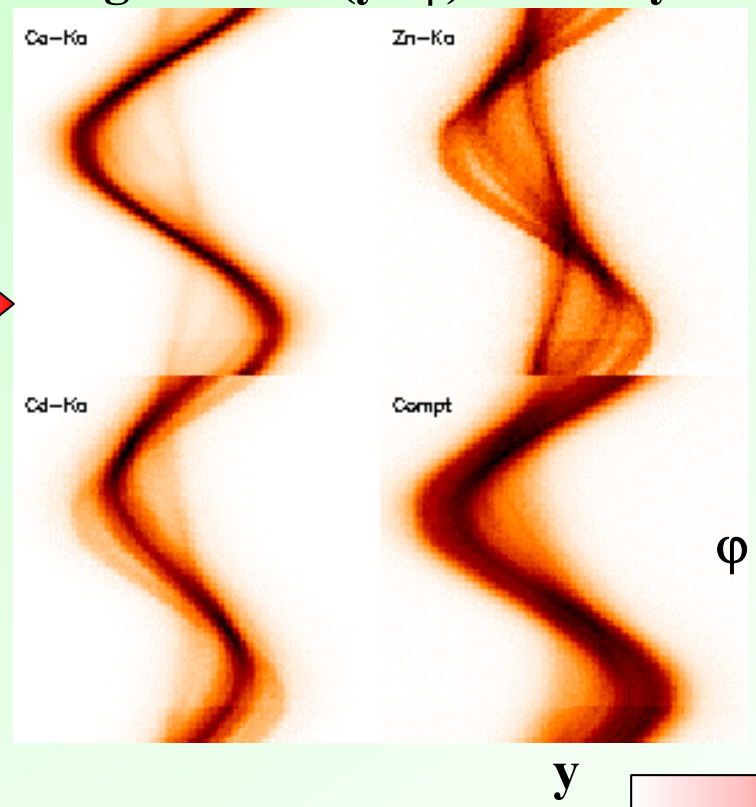
Electron micrograph
A: compartment cell
B: pigment cell
C and D: signet ring cell

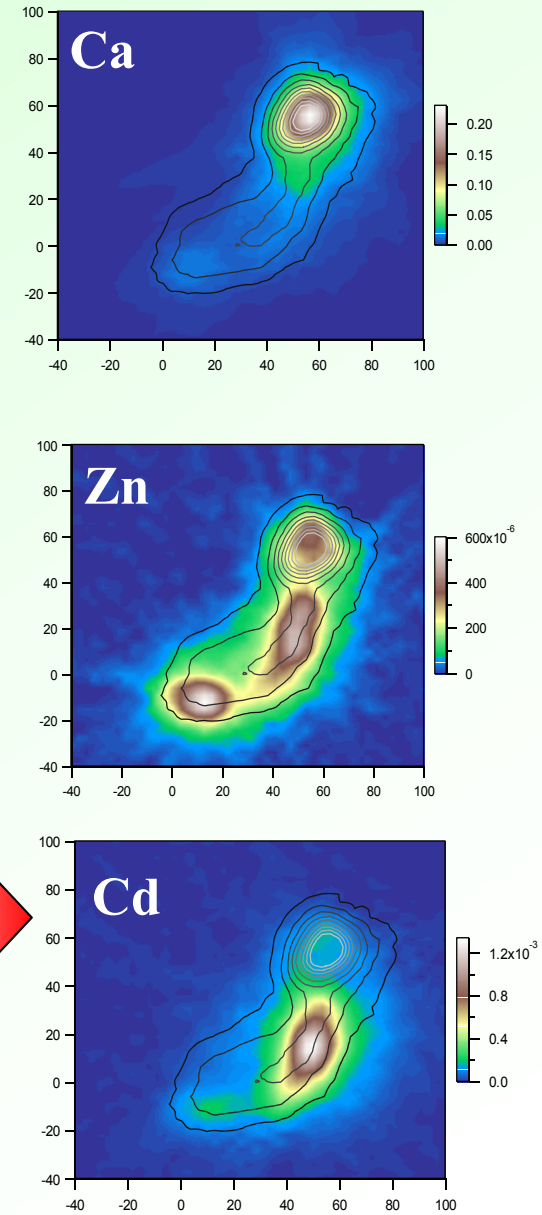
Scanning micro-XRF, 2D/3D internal elemental distribution

Fluorescence tomography



Sinogram: 2D (y- φ) intensity map





Several slices: complete 3D distribution, time-consuming

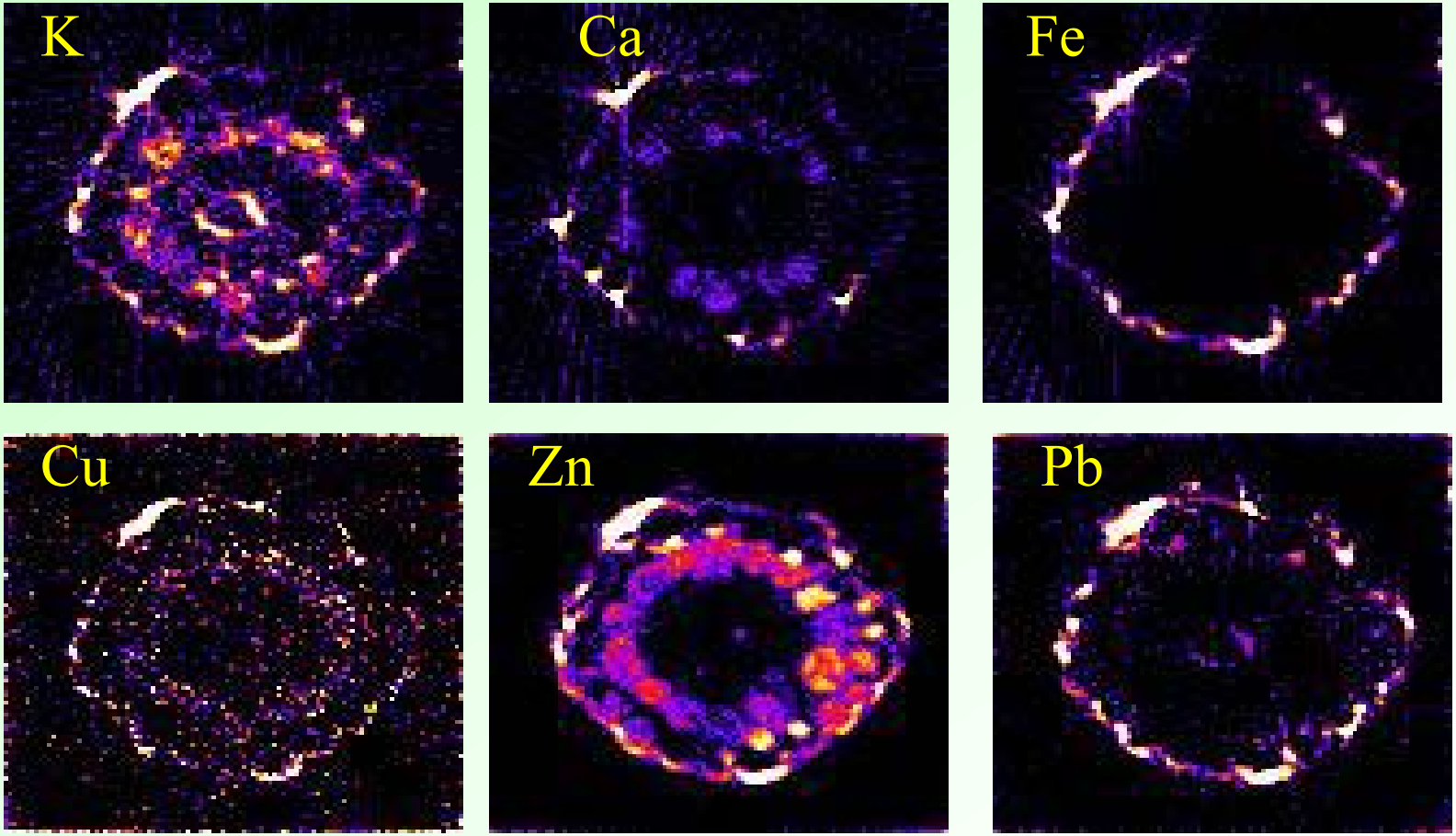
Reconstruction algorithm 2D, (x-y) internal intensity (concentration) distribution

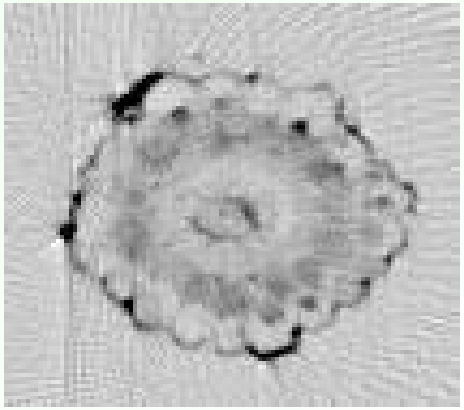
Fluorescence tomography, biological application

W. Schröder, FZ Julich, Ch. Schroer, T.F. Günzler, B. Lengeler, RWTH Aachen, A. Simionovici, CNRS

Study of ion transport in plants

Mycorrhizal root of tomato plant root - Ø < 0.5 mm; resolution ≈ 1 µm



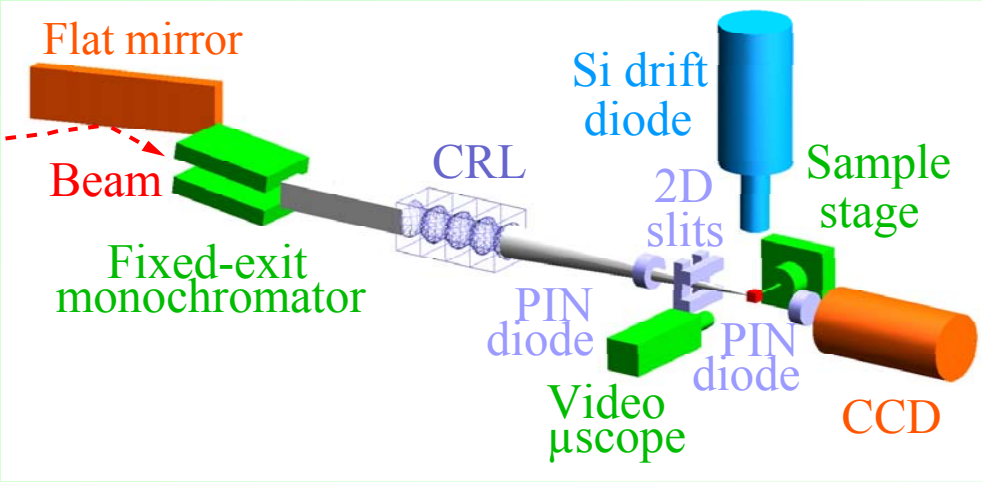


Transmission

Fluorescence tomography, biological application
Search for ET life on micro-meteorites

L. Lemelle, Ph. Oger, Ph. Gillet, ENS Lyon, France

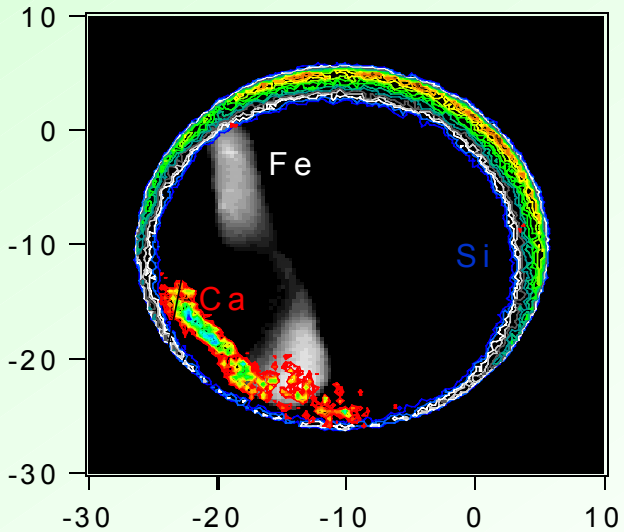
A. Simionovici, M. Chukalina *, B. Golosio, Ch. Rau, ID22, J. Susini, ID21, ESRF

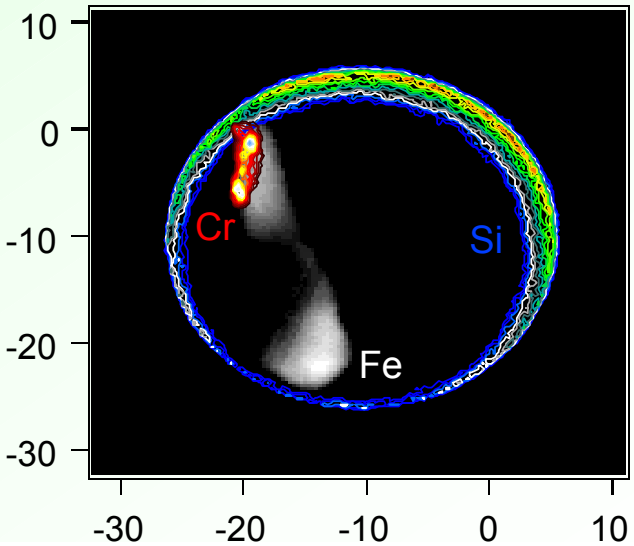


Non-destructive imaging of carbonate sites of formation of bacteria-like remnants - on mineral surfaces, w/o contamination

Complementary to IR, SEM/TEM investigations

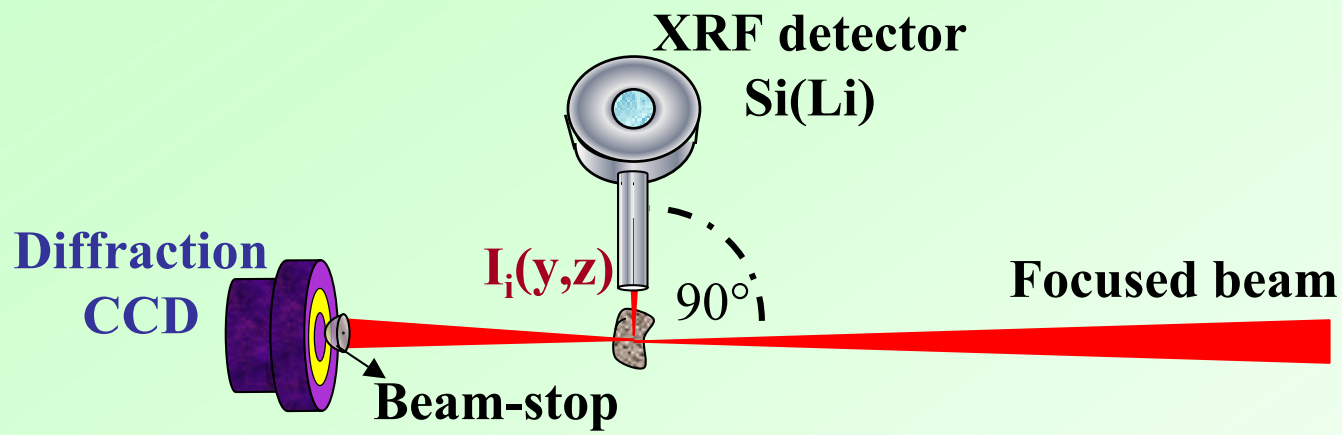
Preparation for MARS return samples - mini-P4 container





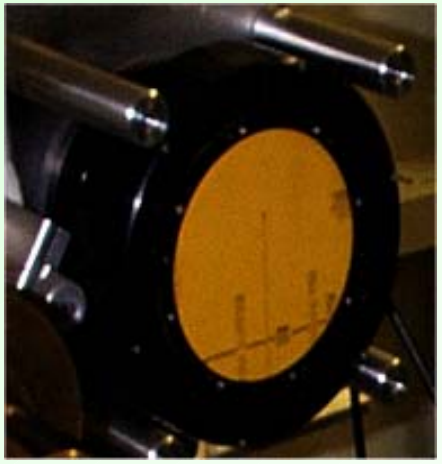
2 µm resolution
2 s/pixel

Scanning μ-XRF + Combined techniques



2D large area low resolution detector in transmission geometry:

Powder diffraction
Small angle scattering



Information about the crystalline structure of the irradiated microspot

simultaneously with micro-XRF

Simultaneous XRF+XRD mapping

Scanning μ-XRF + μ- XRD

Effect of Sr to the evaluation and structure of bone

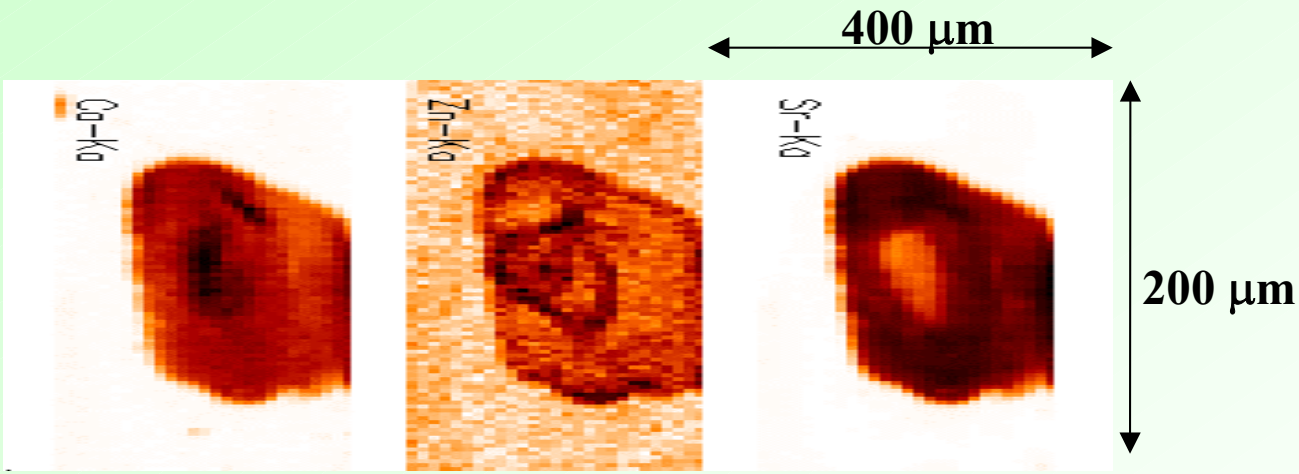
In collaboration: S.C. Verberckmoes, G.J. Behets, A. R. Bervoets, L. Oste, M. E. De Broe, P. C. D'Haese, Dep. of Nephrology-Hypertension, Univ of Antwerp, K. Janssens, Dep of Chemistry , Univ of Antwerp, Belgium, S. Bohic, ID22, ESRF, France

Background :

- **Sr accumulation in bone from dialysis patients of renal failure?**

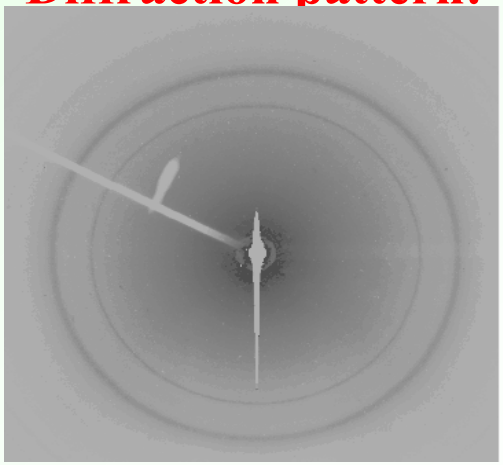
Aim of the study:

- **Localization of Sr**
- **Does Sr alter the bone mineral ? How? Why?**



XRF elemental maps of trabecular bone

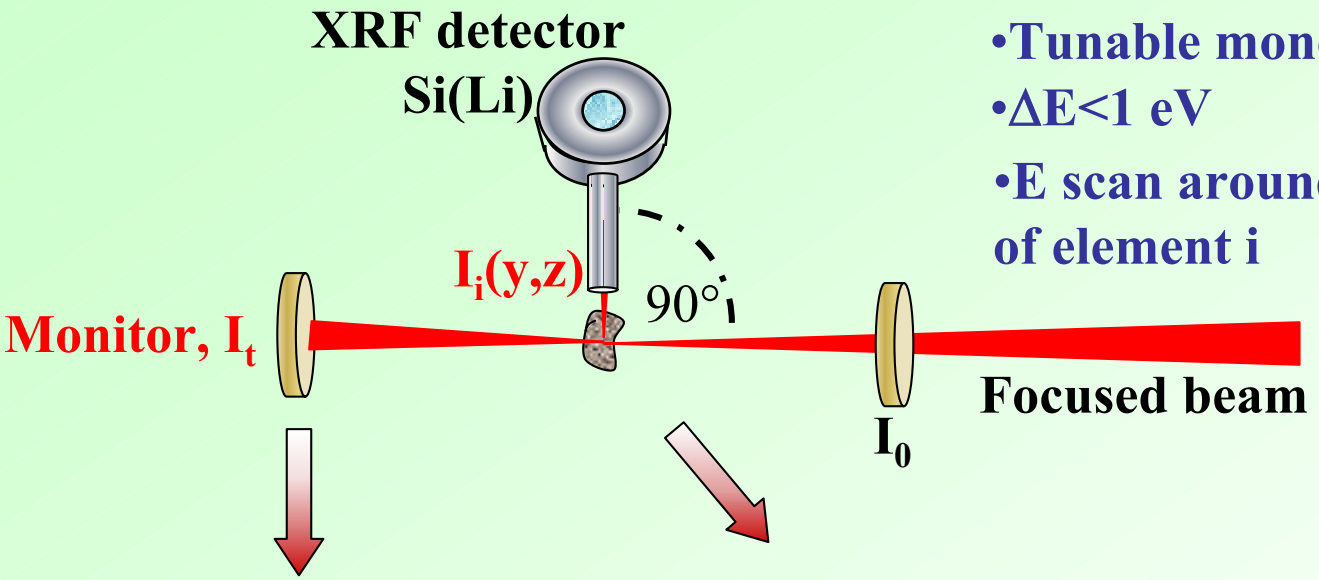
Diffraction pattern:



Information about crystallinity

- **10 μ m thick bone section of rats suffering from chronic renal failure induced by 12 weeks daily oral dose (0.3g Sr/100ml water) -> induced osteomalacia.**
- **E: 17 keV, spot-size, VxH: 2x15 μm^2, LT: 2 s/pixel, CRL of 56 lenses**

Scanning μ-XRF + Combined techniques



- Tunable monochromatic beam
- $\Delta E<1$ eV
- E scan around the abs. edge of element i

$I_t(y,z)$
Transmitted intensity

Transmission mode:

$\mu x(y,z)=\ln(I_t/I_0)$

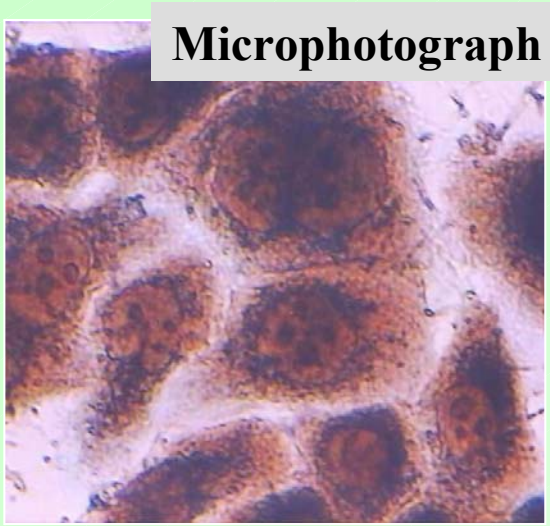
$I_i(y,z)$
Characteristic X-ray line int. of element i

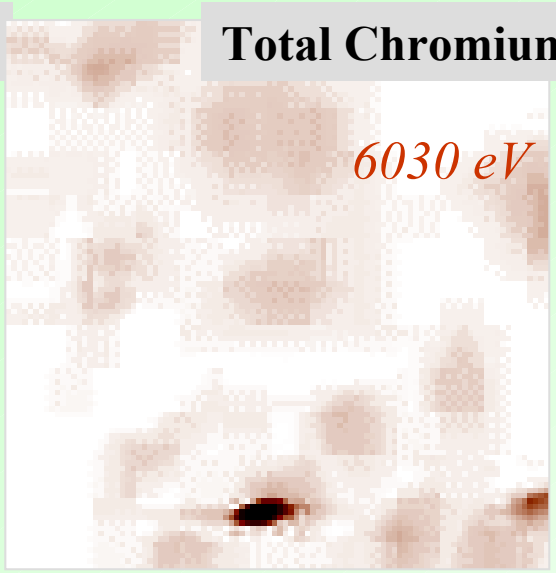
Fluorescence mode:

$\mu x(y,z)\approx I_i/I_0$

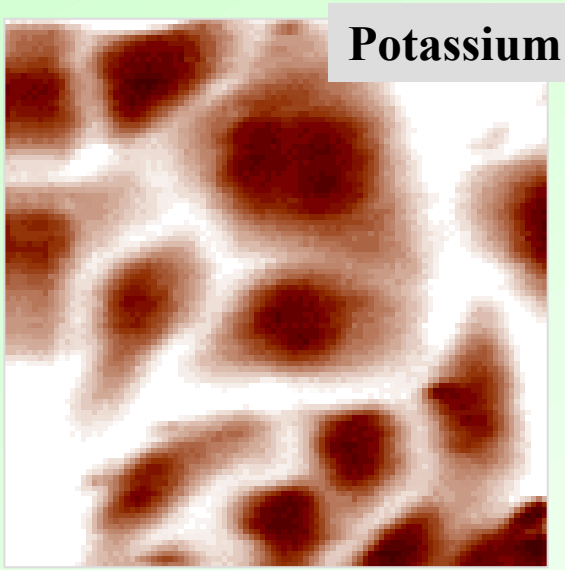
Information about chemical speciation of the micro-spot, μ-XAS

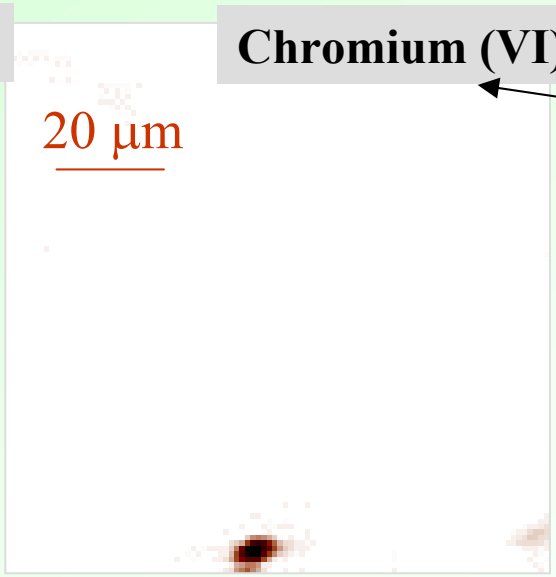
Chemical mapping: chromium oxidation states in single-cells

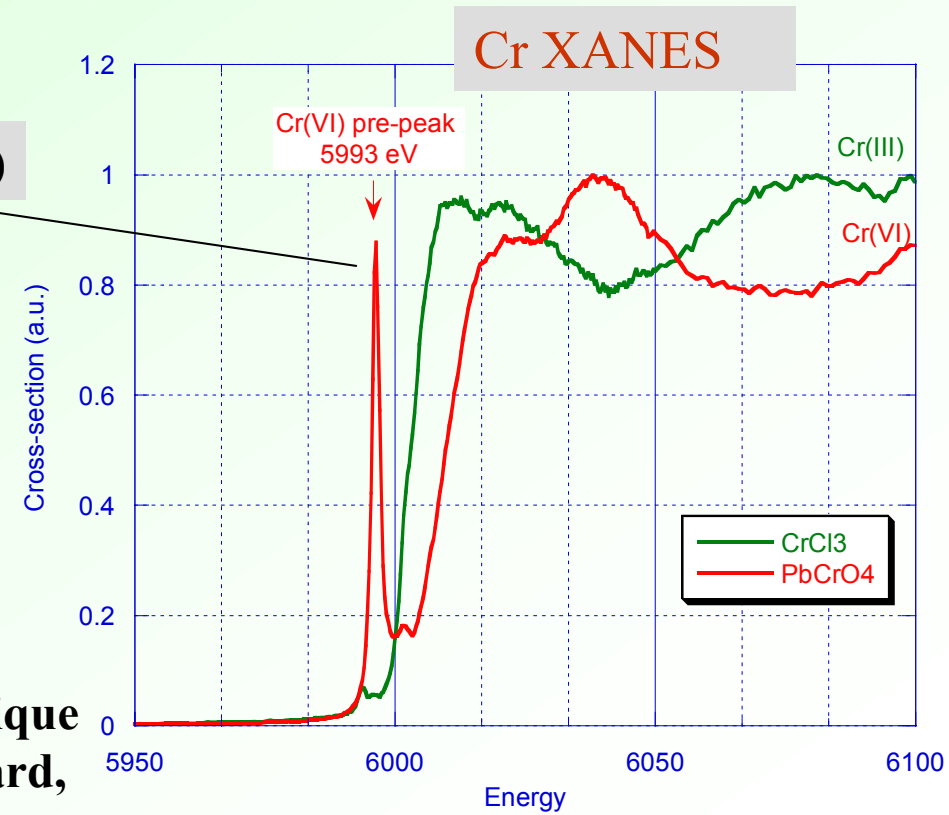




- **Human ovarian cells exposed in vitro to 1 µg/ml $PbCrO_4$**
- **Freeze-dried sample**
- **X-ray microprobe size : 1 x 3 μm^2**
- **Field of view :100 µm x 100 µm**

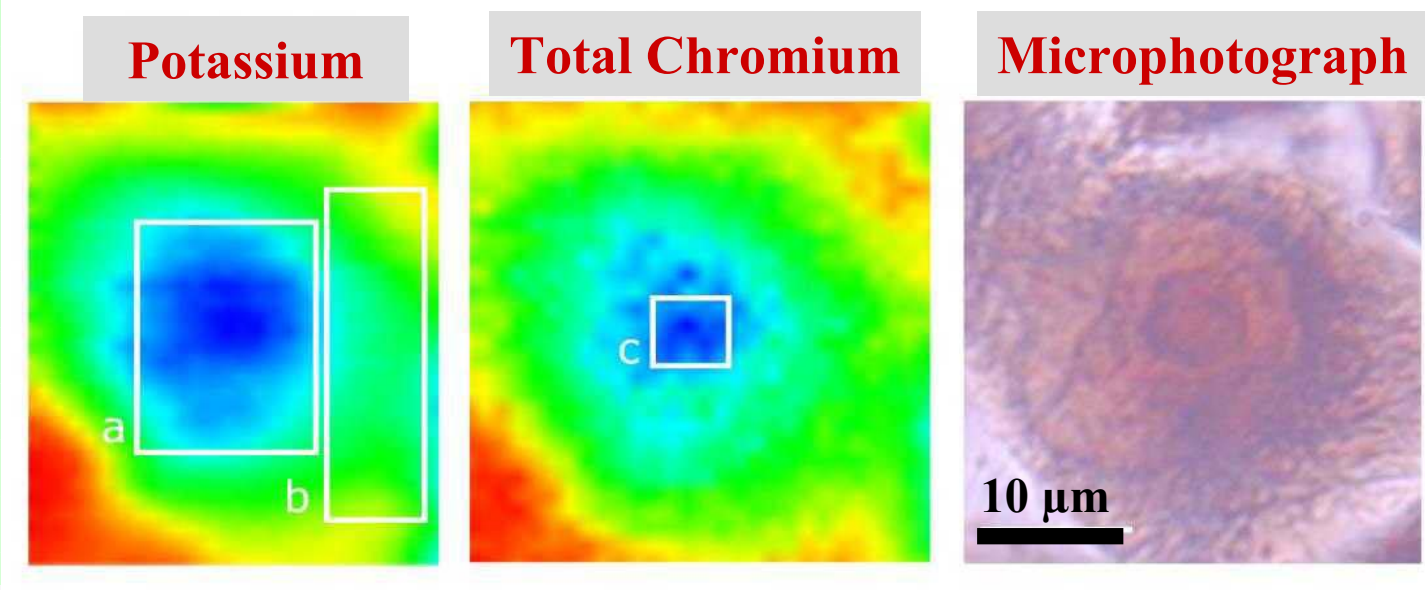






R. Ortega, G. Devès, Lab. de Chimie Nucléaire Analytique et Bioenvironnementale, Gradignan, France & B.Fayard, J. Susini, ESRF- ID21, Grenoble

Chemical mapping: chromium oxidation states in single-cells



Cr/K ratio

a: nucleus	28.0
b: cytosol	31.1
c: nucleolus	26.4

- Cell exposure to low solubility ($PbCrO_4$), and soluble (Na_2CrO_4), Cr(VI) compounds results in intracellular accumulation of reduced forms of Cr.
- Reduced forms of Cr are homogeneously distributed within the cell volume, including the cell nucleus.
- Cr(VI) was observed in the cell environment (aggregates) only after $PbCrO_4$ exposure
- The stronger carcinogenicity of low solubility chromate compounds vs soluble compounds may derived from the combinative genotoxic effects of intracellular Cr (DNA bound ?) and long term exposure to a strong oxidant, Cr(VI).

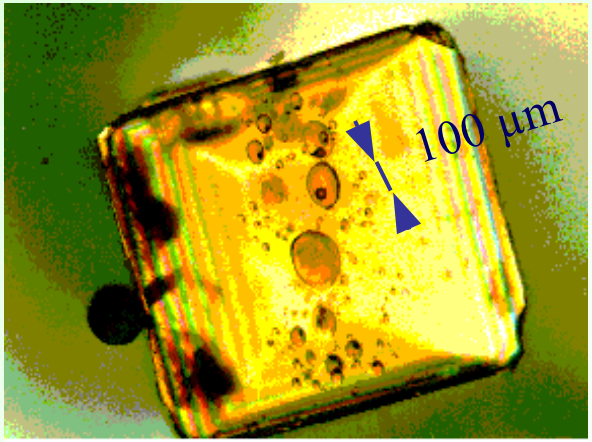
Scanning µ-XRF + Combined techniques

Speciation of Fe in silicate glasses by µ-Xanes

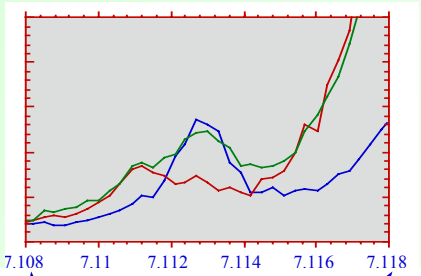
M. Bonnin, N. Métrich, JP Duraud, CEA, Paris, A. Simionovici, ID22, CNRS

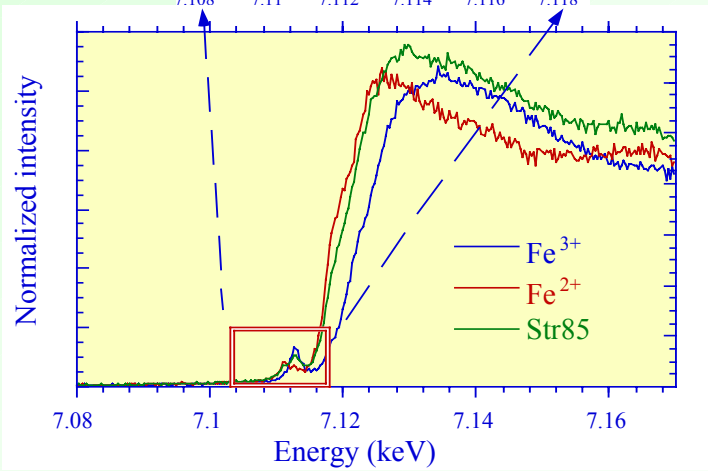
Redox states of Fe/S - control mineralogical phases of magma
- fluid inclusions are magma depth witnesses (1100 - 1300 °)
- S degassing - environmental key parameter (Stromboli: 800 t/day)

- **spatial distribution of $Fe^{2+,3+}$**
- **ref. point for oxidation state**
- **pre-peak serves as quant. par. for Fe^{3+}/S Fe**

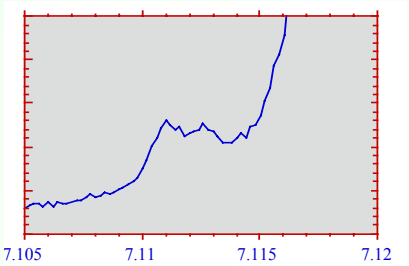


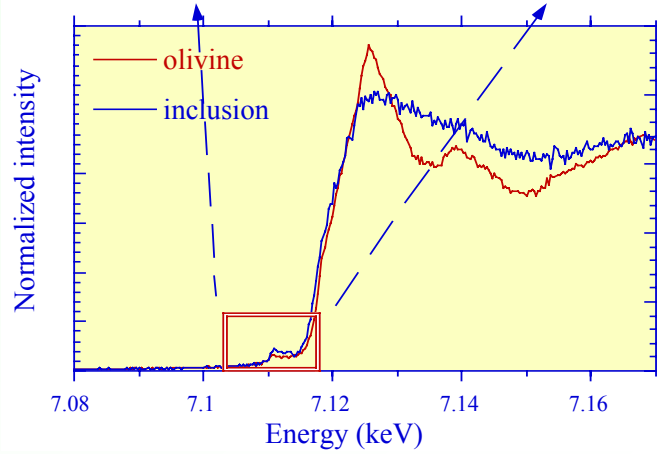
Glass standards containing Fe
Lava melts at 1300°C
Close to glass inclusions





Inclusion from
Piton de la Fournaise
Host: olivine





Scanning μ-XRF + Combined techniques

Environmental application, investigation of single fly ash particles

In collaboration: C.M. Camerani, B.M. Steenari, O. Lindquist Chalmers Univ. , Göteborg, Sweden, B. Golosio, S. Ansell, A. Simionovici, ID22

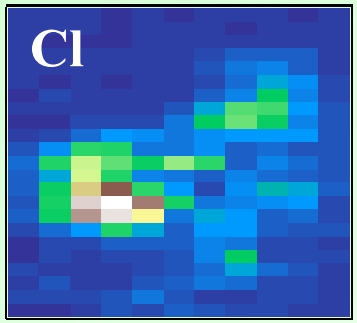
Aim of the study:

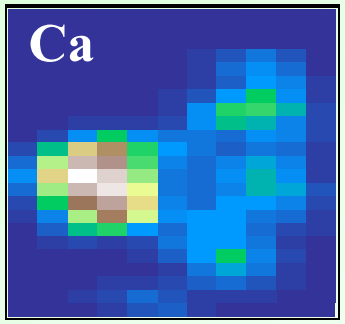
- During combustion large amount of fly ash is created
- Fly ash is a potential danger for the environment
-
- Prediction of the short and long term fate of heavy metals in fly ash particles
- Influence of the chemical speciation of the different elements, crystal structure and porosity of the matrix on the weathering rate
- Toxicity depends on the elemental concentration and speciation

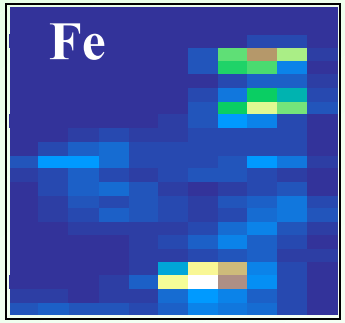
Scanning μ-XRF + Combined techniques

Environmental application, investigation of individual fly ash particles

In collaboration: C.M. Camerani, B.M. Steenari, O. Lindquist Chalmers Univ. of Techn., Göteborg, Sweden, B. Golosio, A. Simionovici, ID22



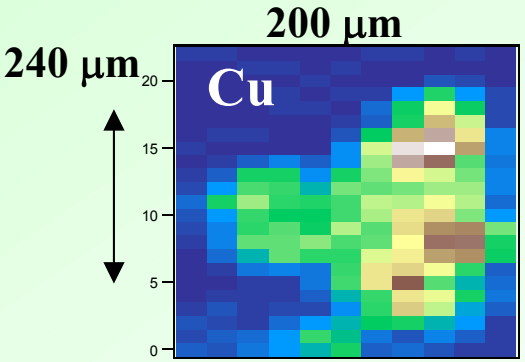


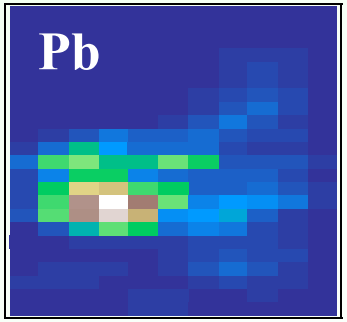


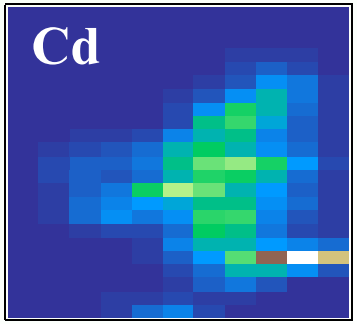
scanning=2D projection of a 3D object!

Intensity distribution reflects the concentration and topological change within the sample

XRF tomography: internal elemental distribution within e.g. slice1 and slice2





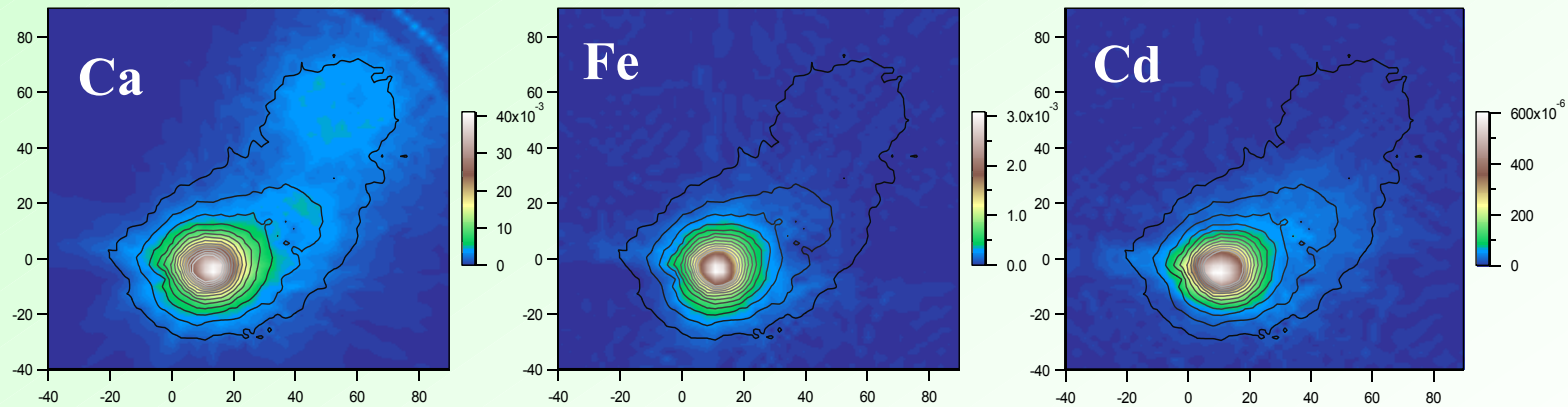


Scanning μ-XRF + Combined techniques

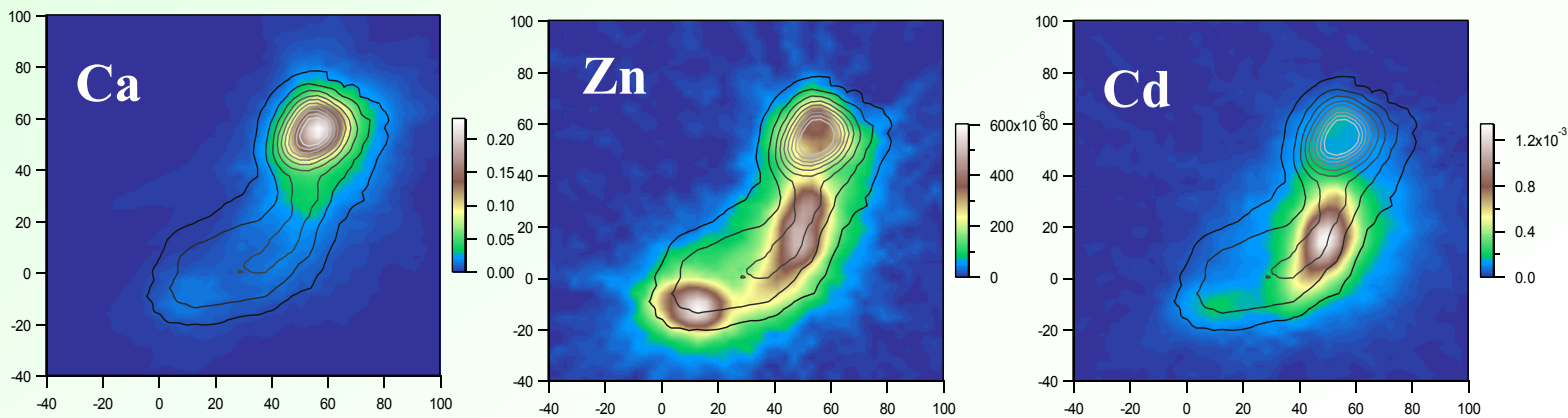
Environmental application, investigation of individual fly ash particles

In collaboration: C.M. Camerani, B.M. Steenari, O. Lindquist Chalmers Univ. of Techn., Göteborg, Sweden, B. Golosio, A. Simionovici, ID22

Internal elemental distribution within Slice2



Internal elemental distribution within Slice1



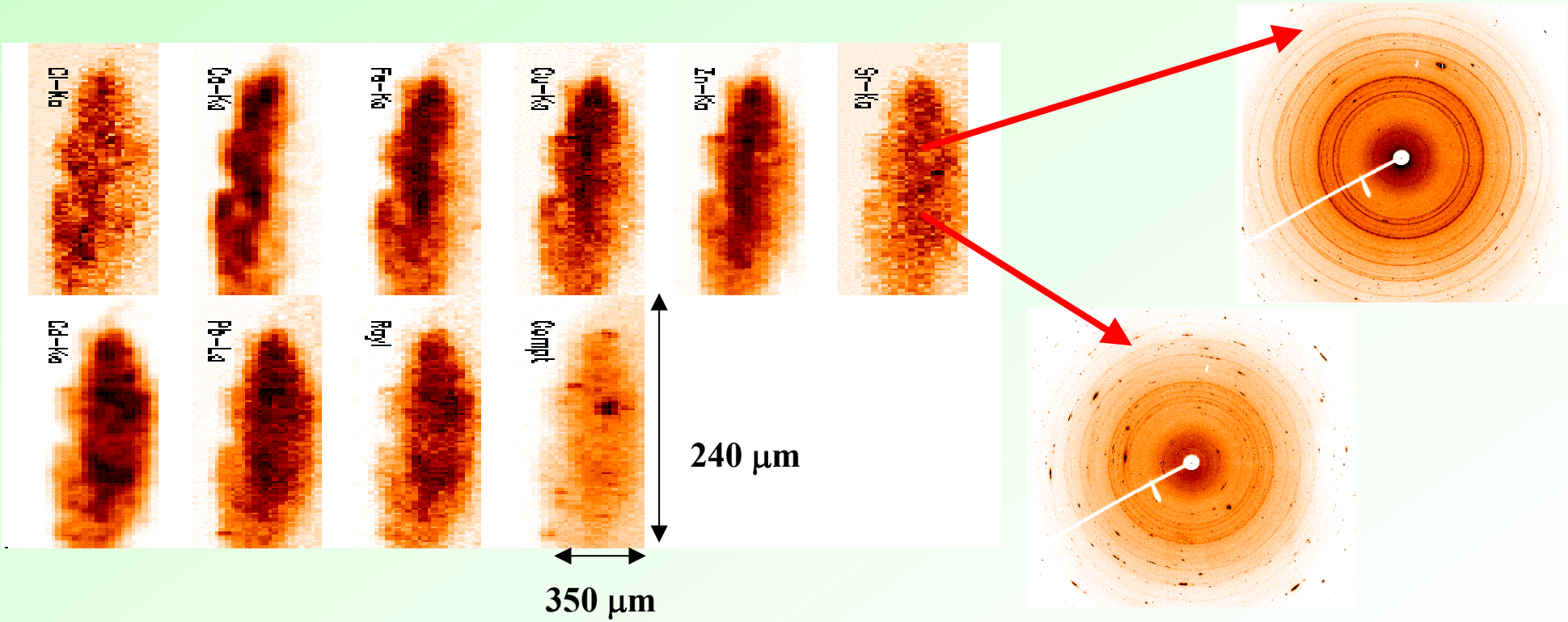
Scanning µ-XRF + Combined techniques

Environmental application, investigation of individual fly ash particles

In collaboration: C.M. Camerani, B.M. Steenari, O. Lindquist Chalmers Univ. , Göteborg, Sweden, B. Golosio, S. Ansell, A. Simionovici, ID22

Crystalline structure: micro-XRD

Scanning-Micro-XRF **Micro-XRD**

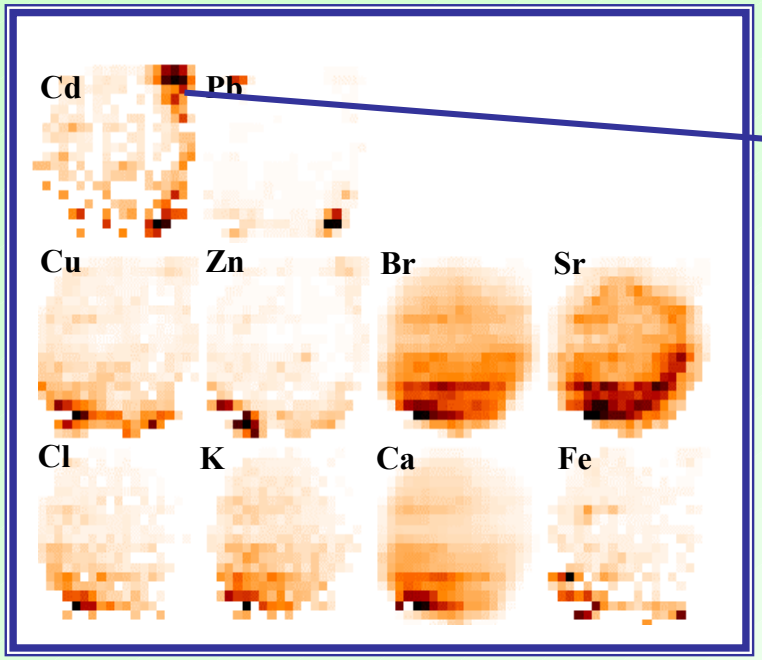


Single waste fly ash particles, LT:6 s, step-size H*V:14*3 µm^2, ID18F/ID22

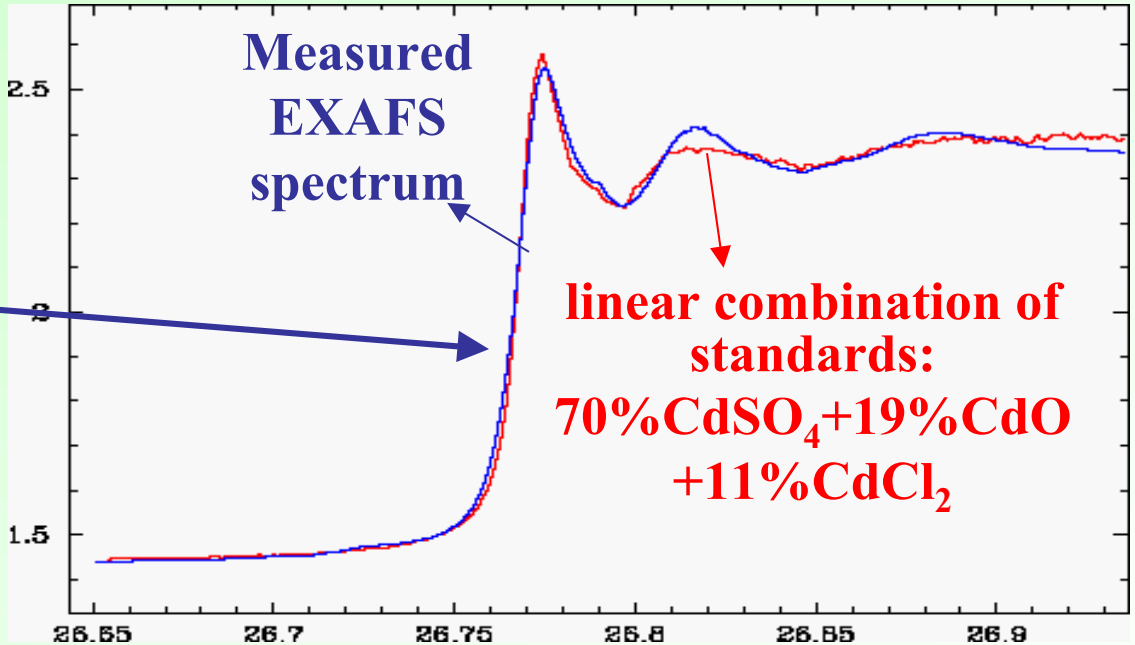
Scanning μ-XRF + Combined techniques

Environmental application, investigation of individual fly ash particles

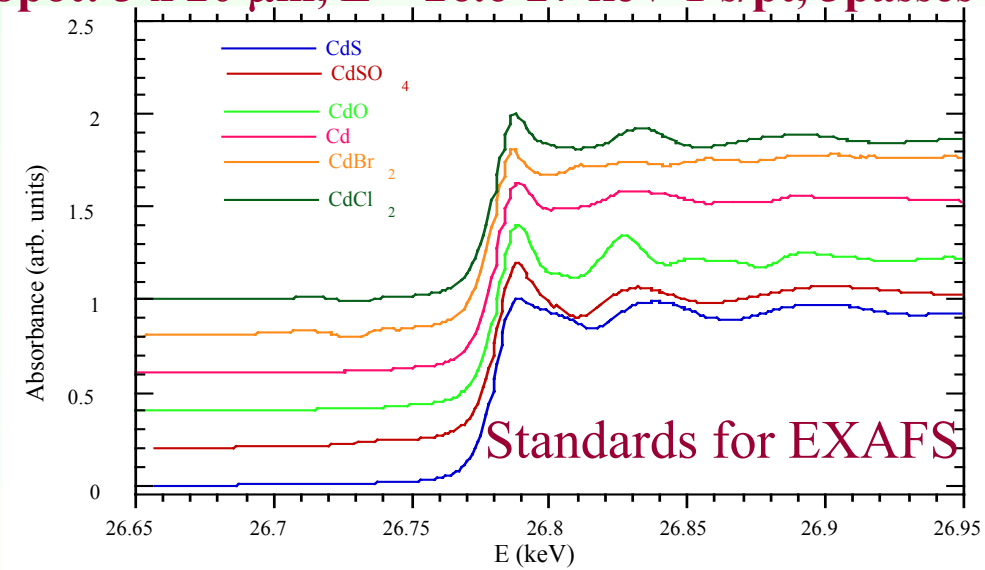
Scanning-μ-XRF



Spot: 8 x 8 μm², E = 27 keV,LT:6 s/pt

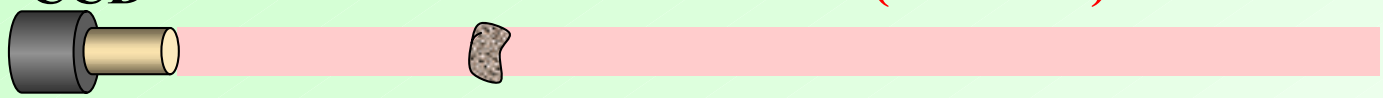


Spot: 3 x 20 μm, E = 26.6-27 keV 1 s/pt, 3passes



Chemical speciation and coordination number of Cd in the chosen pixel: μ -EXAFS

Scanning μ-XRF + Combined techniques



•Full (1*1 mm^2) beam

High resolution CCD:

•absorption (phase contrast) imaging

•absorption tomography: 3D linear absorption coefficient distribution

•Tunable monochromatic beam

•$\Delta E<1$ eV

•E scan around the abs. edge of element i

•Dual energy tomography: 3D elemental ditsribution of a chosen element

•XANES imaging: stack of absorption images around the abs. edge of a given element

Study of Chernobyl hot-spots

In collaboration with B. Salbu, O. C. Lind, T. Krekling, Agricultural Univ. of Norway, Norway
K. Janssens, L. Gijsels, Univ of Antwerp, Belgium
A.Simionovici, CNRS

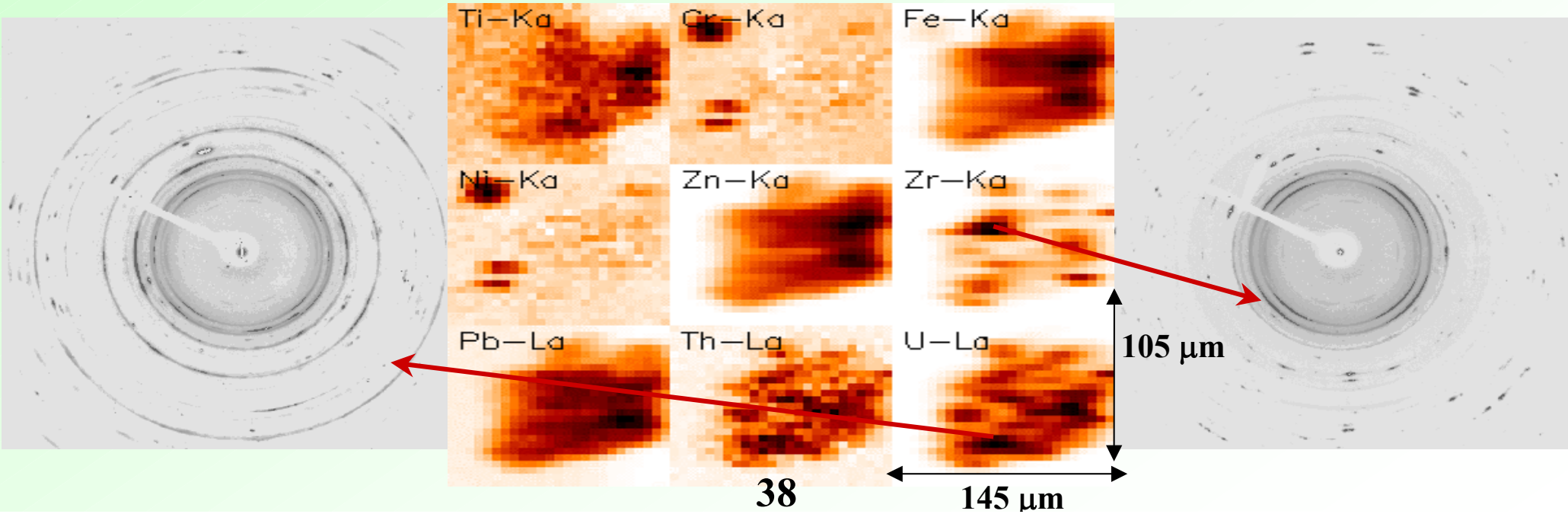
Background:

- **1986 Chernobyl accident**
- **Release of high amount of radioactive fuel particles**

Aim of the study:

- **Prediction of the short and long term consequences in the environment**
- **Influence of the oxidation state of U, that of the crystal structure and porosity of the particles on their weathering rate**

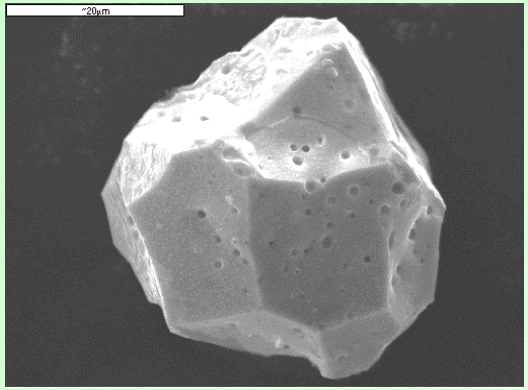
Individual particle, E: 28 keV, spot HxV: 2x5 µm^2, LT:20 s/pixel, simultaneous XRF+XRD mapping, CRL of 140 lenses, ID18F



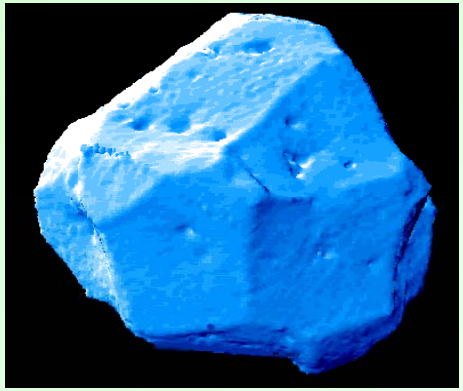
Study of Chernobyl hot-spots

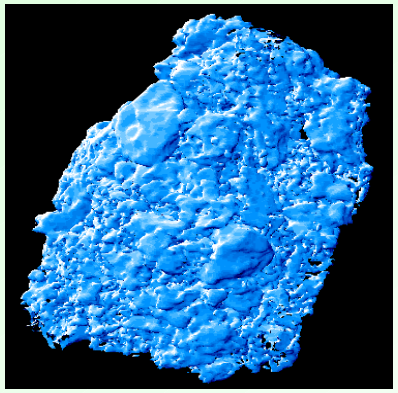
B. Salbu, O. C. Lind, T. Krekling, Agricultural Univ. of Norway, Norway, K. Janssens, Univ of Antwerp, Belgium, A.Simionovici, CNRS, Lyon, France, C. Rau, ESRF, Grenoble, France

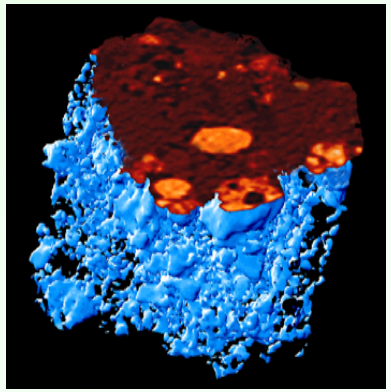
SEM Image



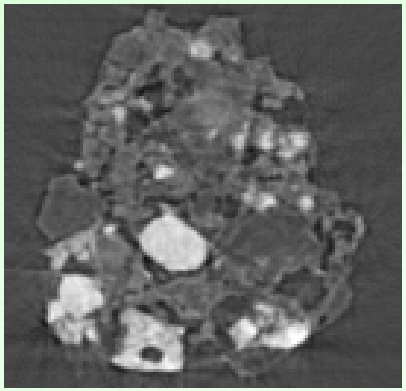
absorption **tomography, 1 µm res., E = 20 keV**



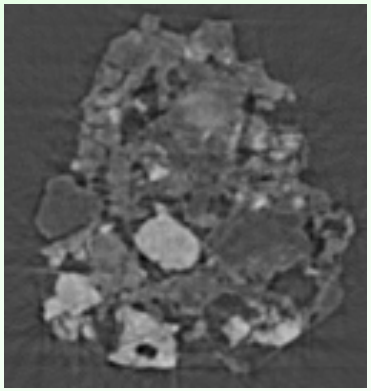




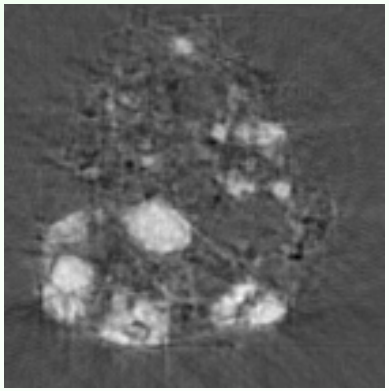
Dual energy absorption tomography: 3D distribution of a given element



E ≈ 17.2 keV



E ≈ 17.1 keV



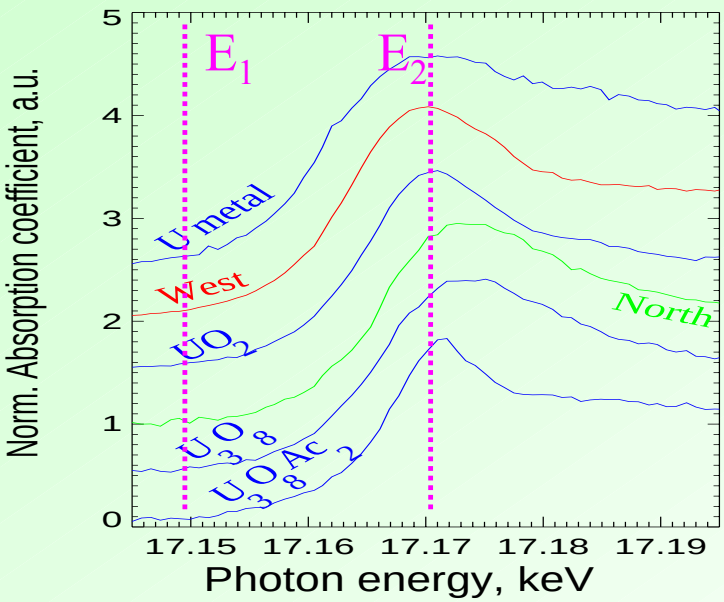
Difference

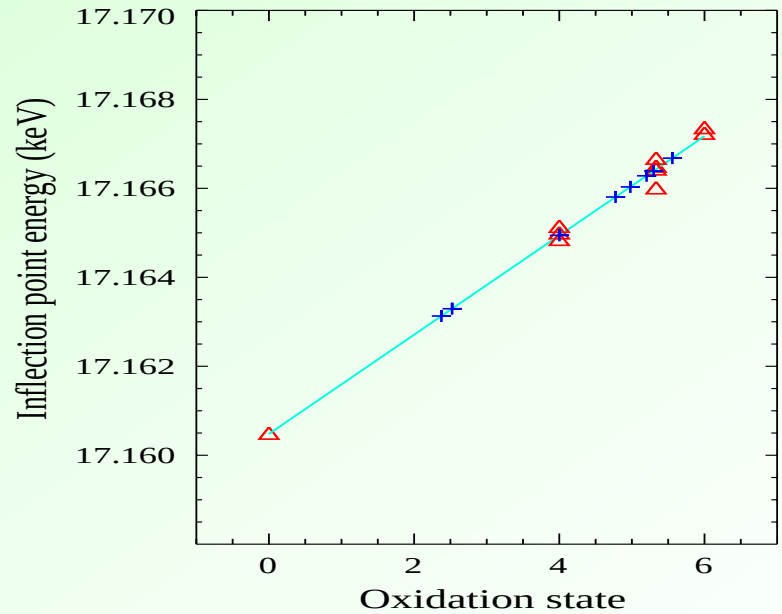
Study of Chernobyl hot-spots

B. Salbu, O. C. Lind, T. Krekling, Agricultural Univ. of Norway, Norway, K. Janssens, Univ of Antwerp, Belgium, A.Simionovici, CNRS, Lyon, France, C. Rau, ESRF, Grenoble, France

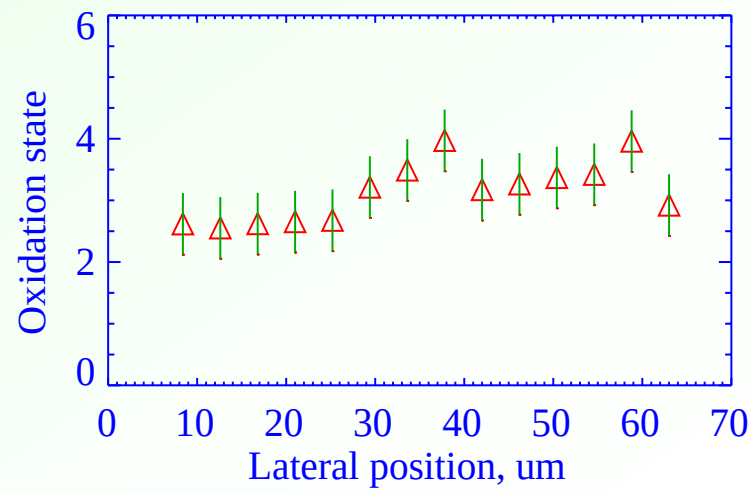
μ -chemical speciation of uranium

calibration: U metal, UO_2 and U_3O_8 ($0^+ – 6^+$)
FWHM ≥ 0.15 eV, dE ≈ 0.8 eV/q
2 x 5 μm, flux $8 \bullet 10^8$ ph/s., 2 - 5 sec./point





L_{III}-edge μ -xanes line scan across a particle



Conclusion

- **Scanning micro-XRF analysis is a powerful method of investigation in different research fields, such as biology, environmental science, geology**
- **It gives information about the 2D elemental distribution and possible correlation among different element**
- **2D non-destructive internal analysis: fluorescence tomography**
- **The combination of different micro-techniques provides more complete information about the sample, e.g. elemental composition, speciation, morphology, crystal structure**

ID21, ID22/ID18F beam-lines of the ESRF

	ID21	ID22
responsible:	J. Susini	
Scientist:	M. Salome	A. Somogyi S. Bohic (ID18F) M. Drakopoulos (ID18F)
BLOM	R. Toucoulou	
Post. Doc.	U. Neuhaussler O. Dhez	
PhD student:		B. Golosio
Techitian:	R. Baker	S. Labouré
Visiting scientist:	B. Fayard (CNRS)	A. Simionovici (CNRS)