

# **X-ray fluorescence analysis**

Tokyo University of Science  
Department of Applied Chemistry

Izumi NAKAI

# Outline of the lecture

- **Introduction to XRF**
- **Characteristics of SR and the advantages in X-ray fluorescence analysis with application examples**

(1) Highly Brilliant X-ray Source

(2) Parallel beam with small divergence

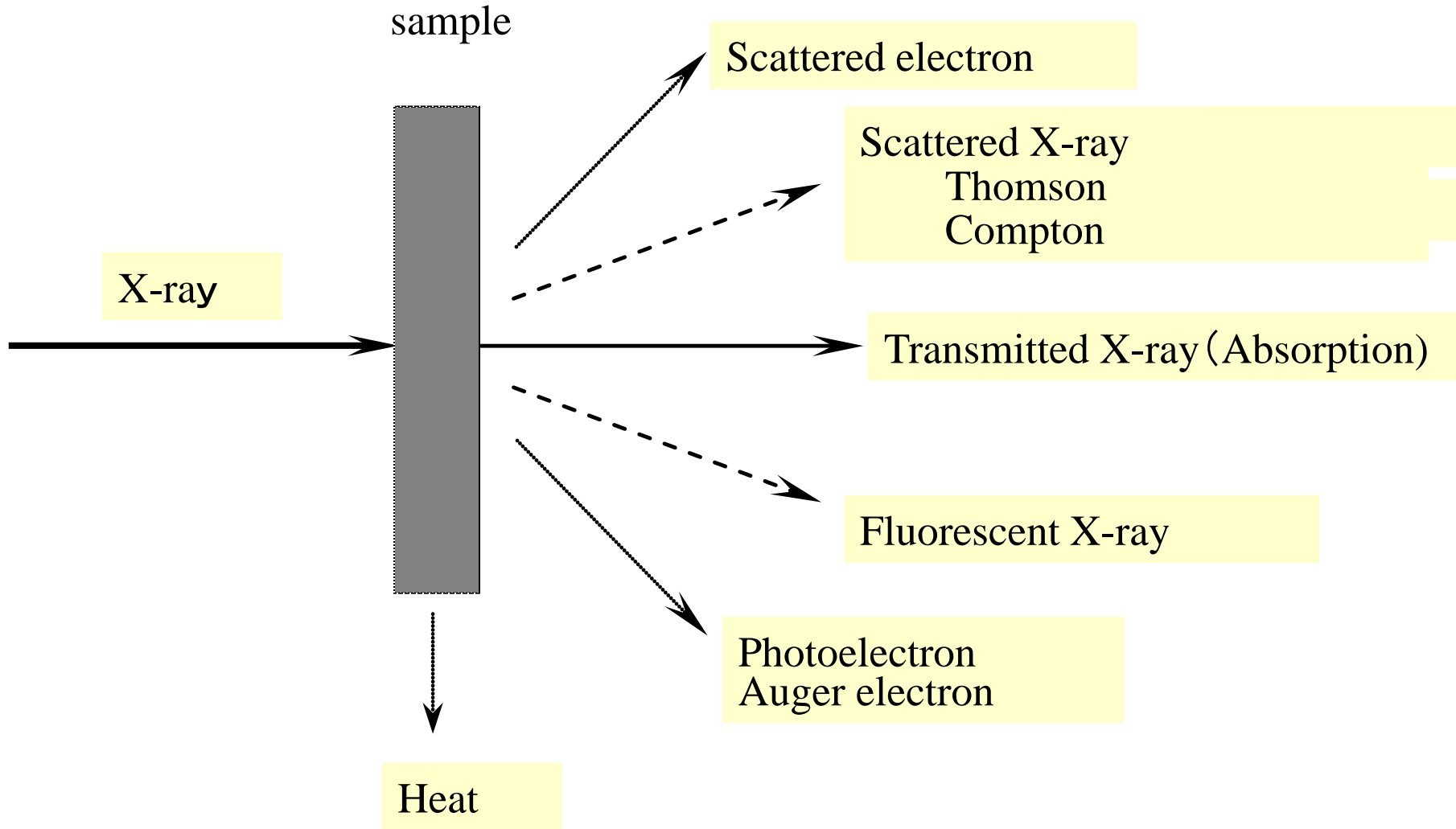
(3) Energy tunability

- Chemical state analysis by Fluorescence –XAFS

(4) High energy X-ray

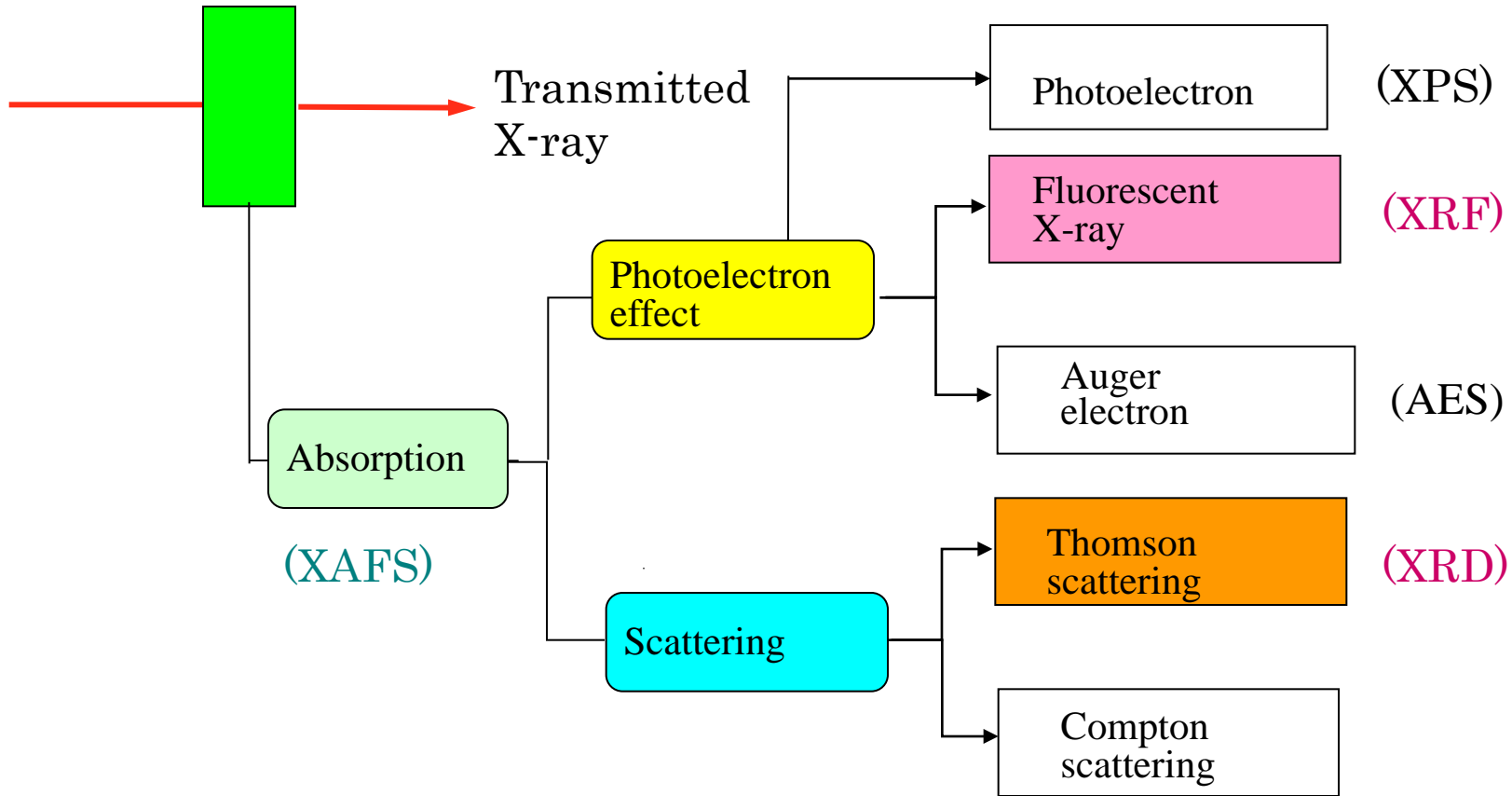
(5) Multiple X-ray analytical technique- A combination of  $\mu$ -XRF imaging,  $\mu$ -XRD, XAFS and SEM

▪ **Conclusion**



Interaction of X-ray with matter

sample



## Interaction of X-ray with matter and X-ray analysis

## Relationship between $\lambda$ and E

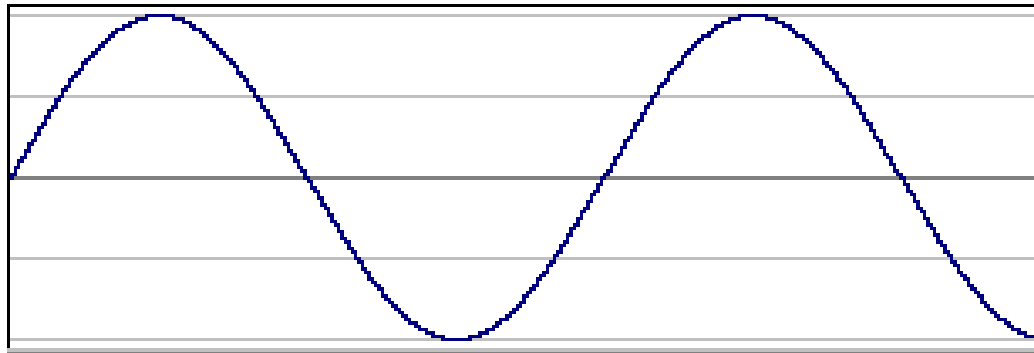
Particle : energy E [keV]

Wave : wavelength  $\lambda$  [Å]

$$E = hc/\lambda = 12.398/\lambda \quad [\text{keV}],$$

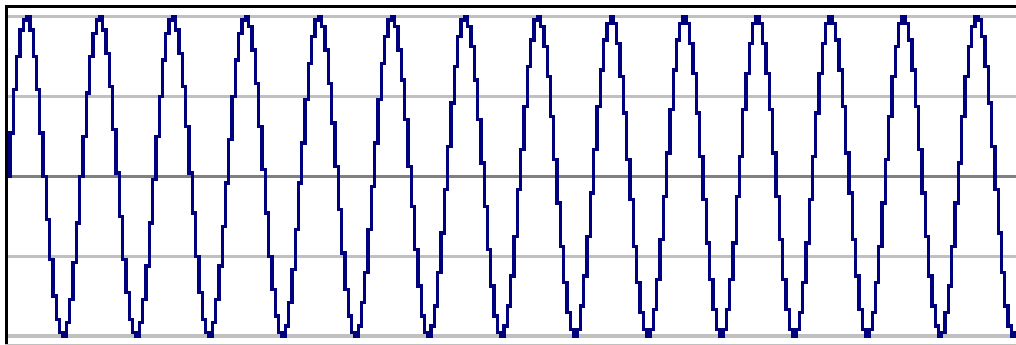
ex.  $1 \text{ \AA} = 12.398 \text{ keV}$

Wavelength  $\lambda$



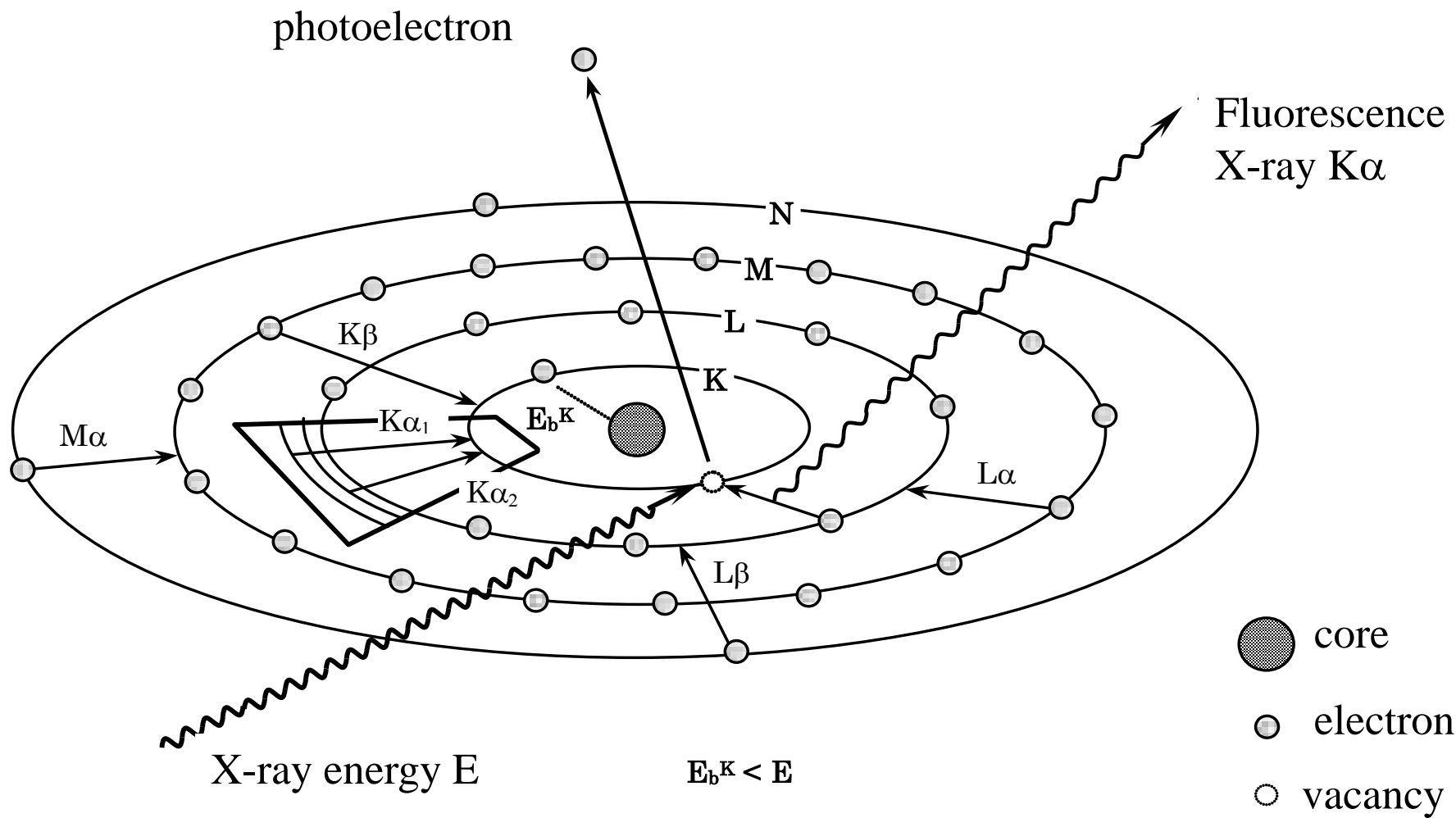
$\lambda = \text{long}$

Energy = low



$\lambda = \text{short}$

Energy = high



X-ray energy  $E >$  Binding energy  $E_b$

Bohr model and emission of X-ray fluorescence

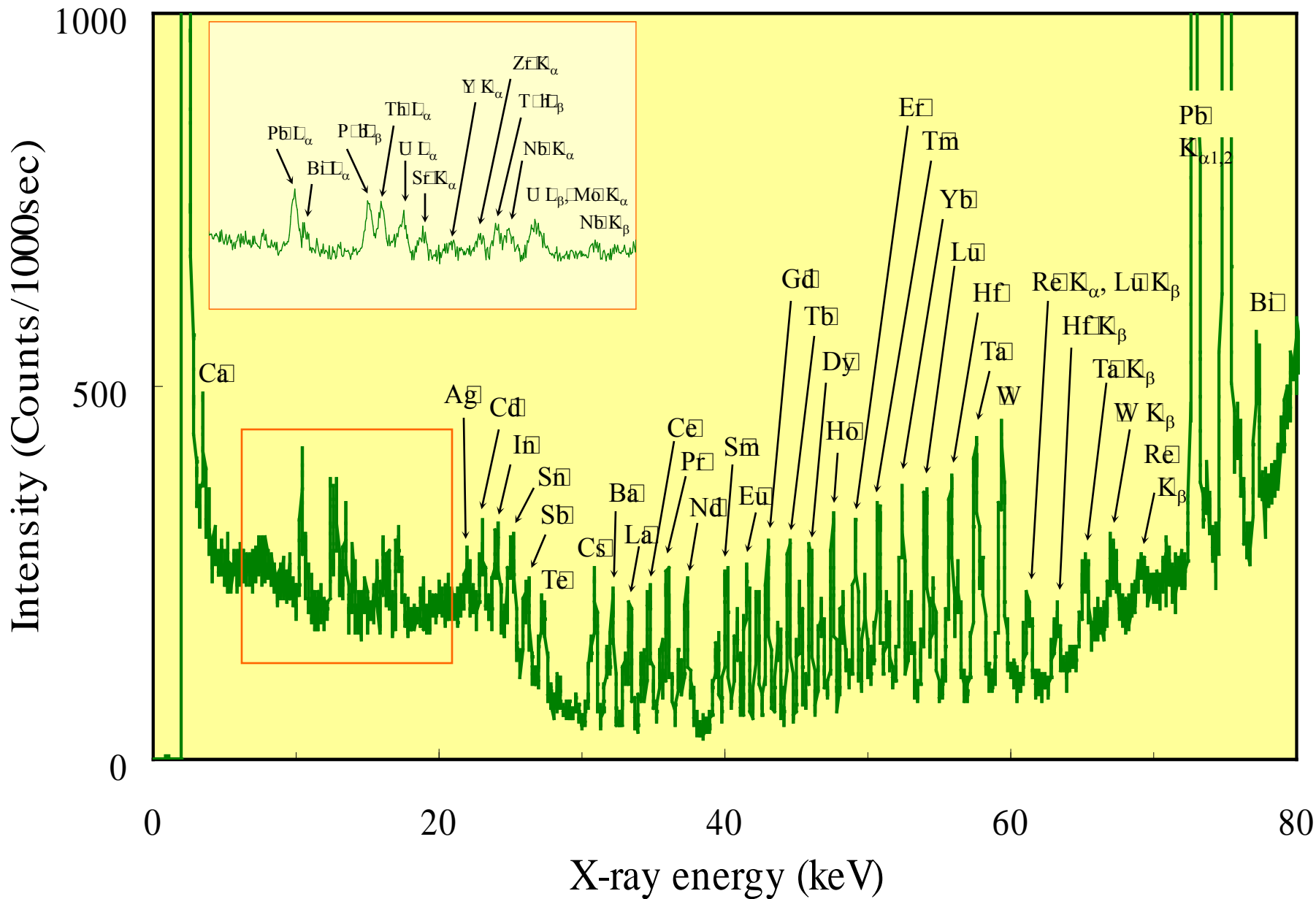
# Principle of X-ray fluorescence (XRF) analysis

**Energy**  $\Delta E$  characteristic to each element

Qualitative analysis


**Intensity** number of X-ray photons  $\rightarrow$  concentration

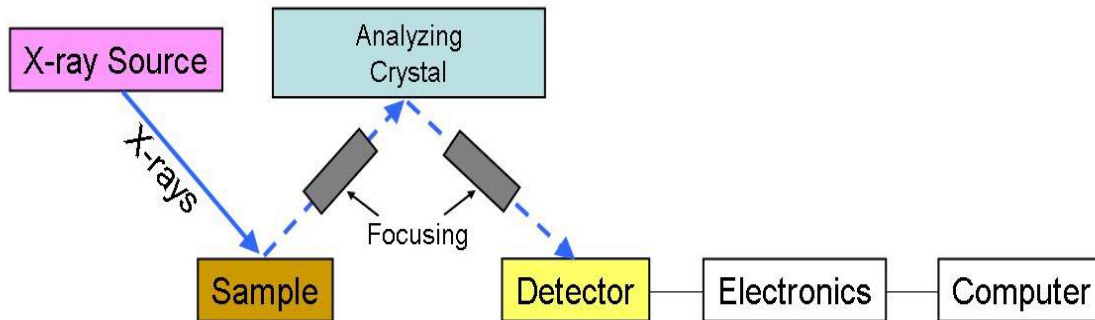
Quantitative analysis



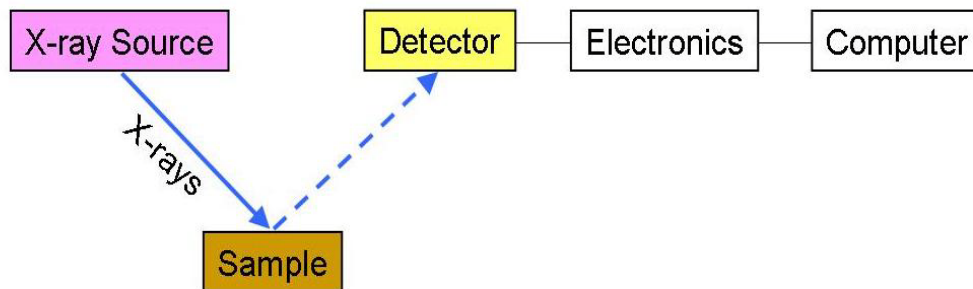
XRF spectrum of **RI**



d-spacing   
Analyzing crystal



(a) WDS



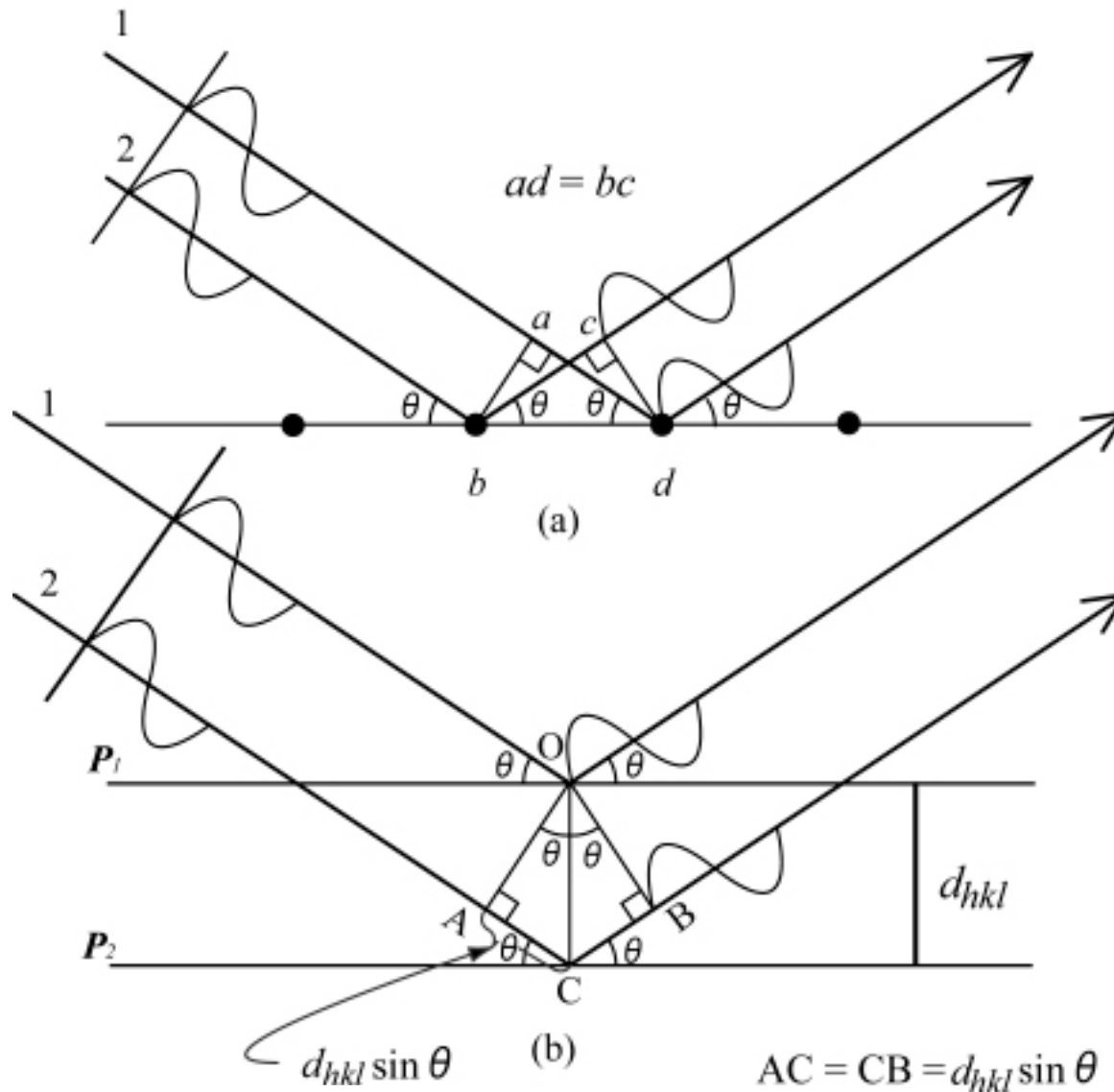
(b) EDS

## XRF analysis

(a) Wavelength dispersive spectroscopy

(b) EDS Energy dispersive spectroscopy

# Principle of analyzing crystal



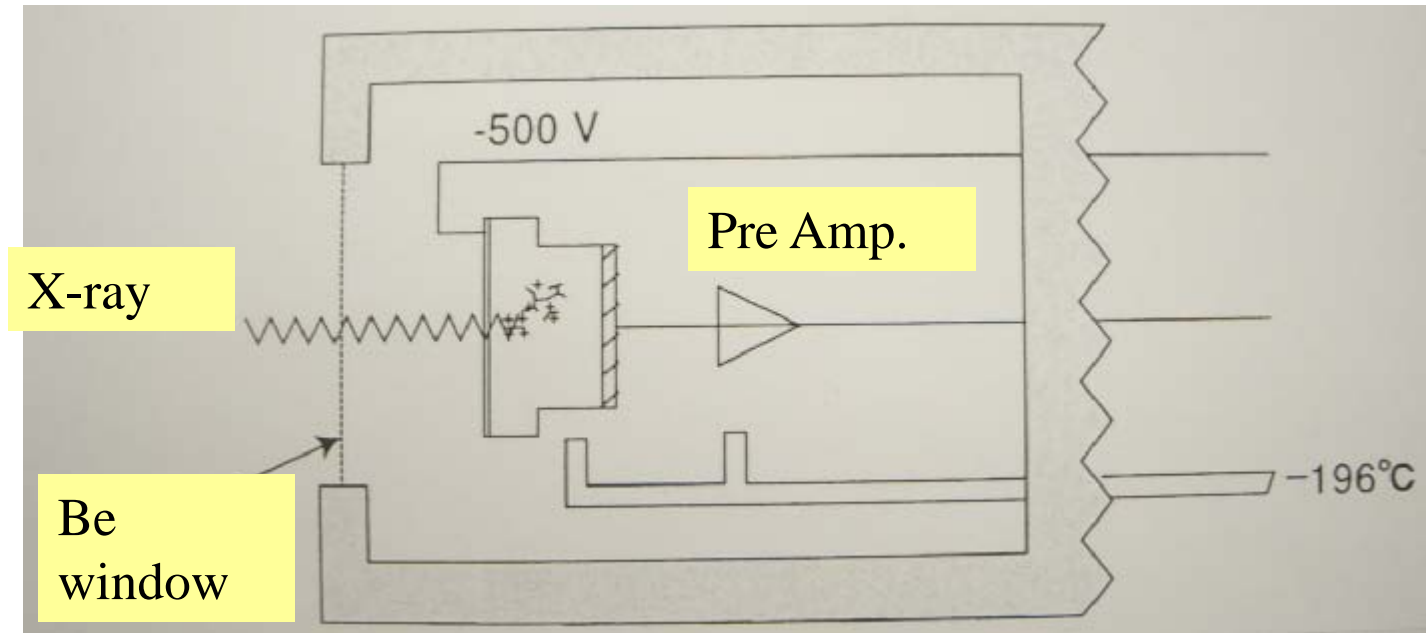
Bragg condition  $n\lambda = 2d \sin \theta$

## 5.1 X-ray Fluorescence Analysis

Commonly used analyzer crystal: LiF, ADP (ammonium dihydrogen phosphate), Ge, graphite, InSb, PE (*tetrakis*-(hydroxymethyl)-methane: penta-erythritol), KAP (potassium hydrogen phthalate), RbAP (rubidium hydrogen phthalate) and TIAP (thallium(I) hydrogen phthalate). In addition, synthetic multilayer is used to detect the light elements in the range Li to Mg.

material	plane	d nm	min $\lambda$ nm	max $\lambda$ nm	intensity	thermal expansion	durability
LiF	200	0.2014	0.053	0.379	+++++	+++	+++
LiF	220	0.1424	0.037	0.268	+++	++	+++
LiF	420	0.0901	0.024	0.169	++	++	+++
ADP	101	0.5320	0.139	1.000	+	++	++
Ge	111	0.3266	0.085	0.614	+++	+	+++
graphite	001	0.3354	0.088	0.630	++++	+	+++
InSb	111	0.3740	0.098	0.703	++++	+	+++
PE	002	0.4371	0.114	0.821	+++	+++++	+
KAP	1010	1.325	0.346	2.490	++	++	++
RbAP	1010	1.305	0.341	2.453	++	++	++
Si	111	0.3135	0.082	0.589	++	+	+++
TIAP	1010	1.295	0.338	2.434	+++	++	++
6 nm SM	-	6.00	1.566	11.276	+++	+	++

**Principle of Si(Li) detector** → a reverse-biased silicon diode.



Si(Li) detector      electron-hole pair → 3.85eV

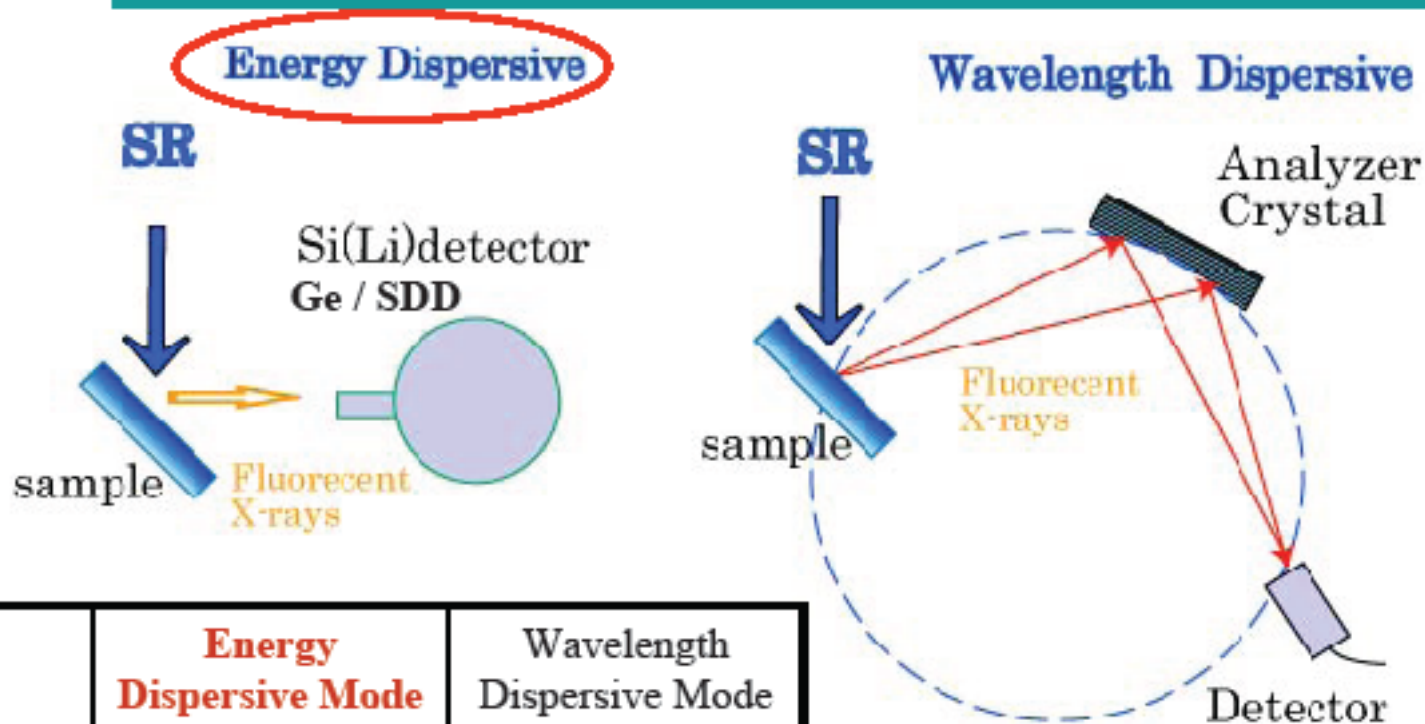
ex. Fe  $K\alpha$  6.400keV     $6400/3.85=1662$  pairs

Bias voltage(-500V) cause currents flow. The charge collected at the anode is converted to a **voltage** by an amplifier. This results in a **voltage pulse that is proportional to** the number of pairs created and thus to **the incident X-ray energy**. The resolution is determined by the energy required to create an electron-hole pair (3.8 eV).



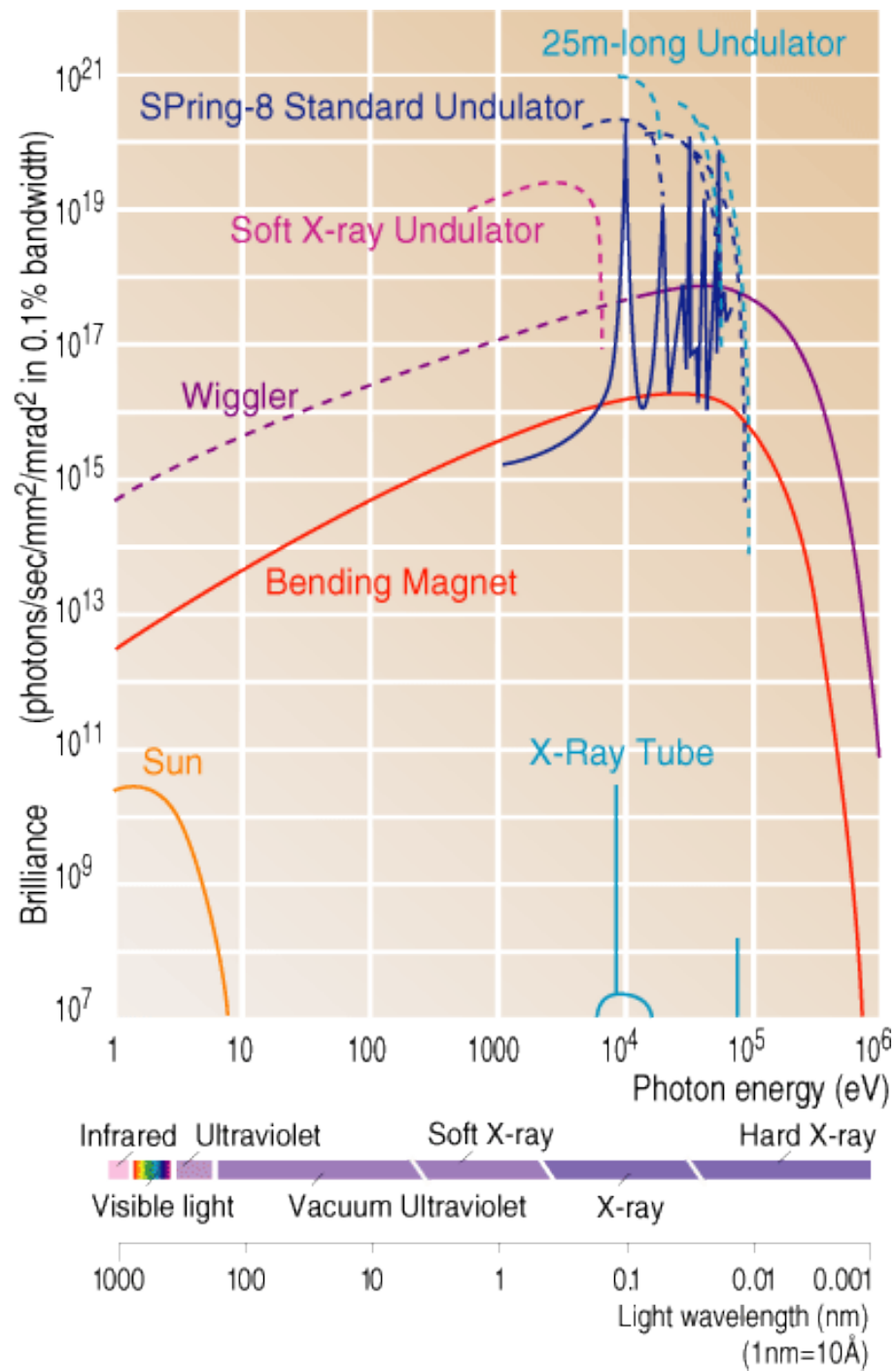
← Slides made by Prof. A. Iida (PF)

## Energy Dispersive Mode vs. Wavelength Dispersive Mode



	<b>Energy Dispersive Mode</b>	Wavelength Dispersive Mode
Advantage	<ul style="list-style-type: none"> <li>• <u>High Efficiency</u></li> <li>• Multi-elemental detection</li> </ul>	<ul style="list-style-type: none"> <li>• High resolution</li> <li>• High S/B</li> </ul>
Disadvantage	<ul style="list-style-type: none"> <li>• <u>Low resolution</u></li> <li>• Scattering background</li> </ul>	<ul style="list-style-type: none"> <li>• Low efficiency</li> </ul>

Characteristics of SR  
and the advantages in  
X-ray fluorescence analysis  
with application examples





# SR Properties and SRXRF

## 1) High Brilliance Source

(small size and high collimation X-ray source)

strong intensity (high density)

=> **signal enhancement**

high collimation

=> **micro beam analysis (focusing optics)**

=> **total reflection XRF**

## 2) Linear polarization

(p polarization +  $90^\circ$  arrangement) => **background reduction**

## 3) White (bending magnet), quasi-monochromatic (Undulator) X-rays

monochromatic X-rays

=> **background reduction**

(monochromator)

=> **selective excitation**

(S/B optimization / Resolving overlapping peak)

continuous energy scanning

=> **XAFS**

(Chemical state analysis)

## 4) High and low energy X-ray excitation

=> **heavy & light trace elements analysis**

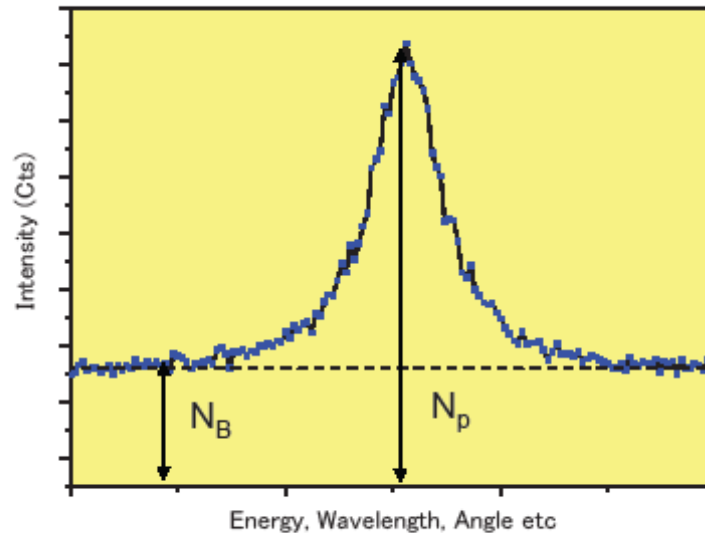


( 1 ) Highly Brilliant X-ray Source

Sensitivity of XRF analysis  
is determined by  $N_p$  and  $N_B$

MDL (Minimum detection limit)

XRF spectrum



Minimum detection  
limit (MDL)

$$k = \frac{3C\sqrt{N_B}}{N_p - N_B}$$

Minimum quantification  
limit (MQL)  $(2k \sim 3.3k)$

$N_p$  increase = Signal increase

→ High brilliance source

High flux source

$N_B$  decrease →

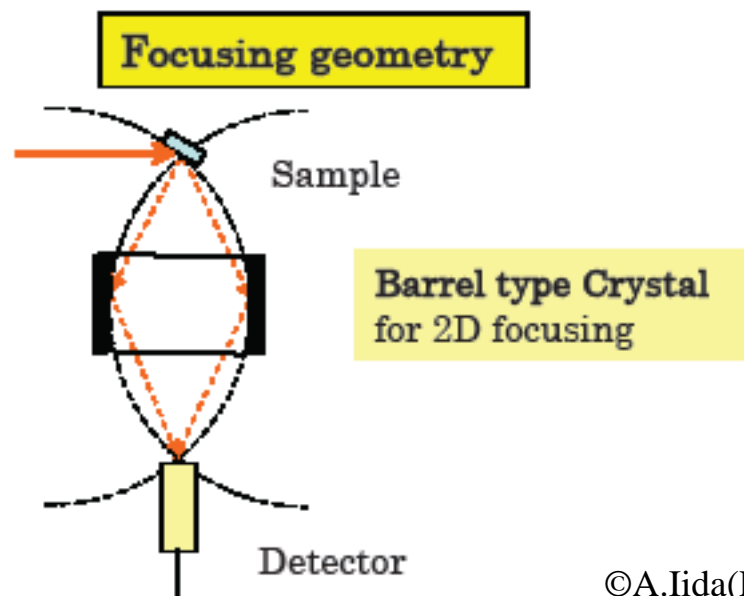
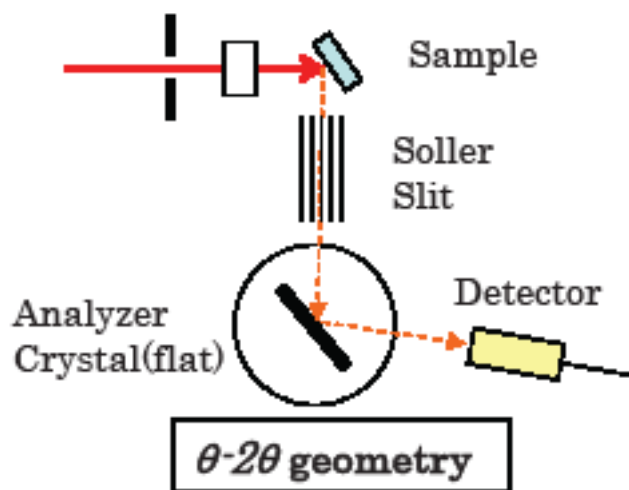
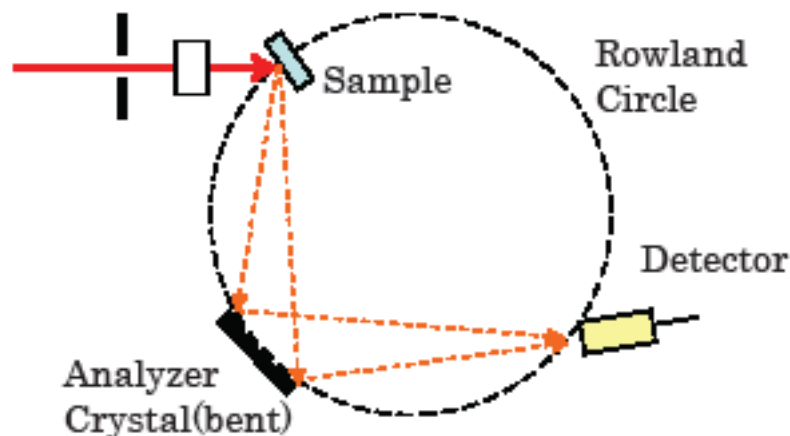
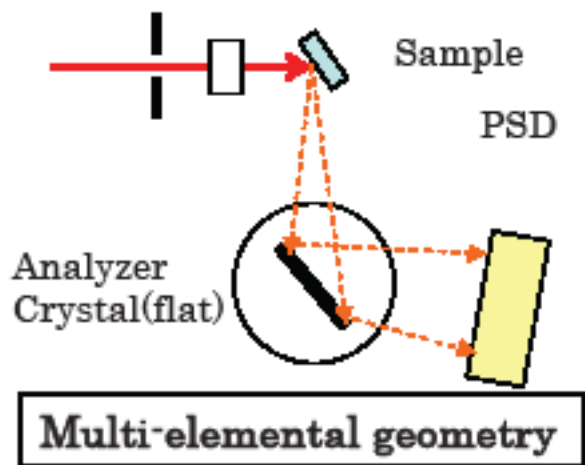
Monochromatic Excitation

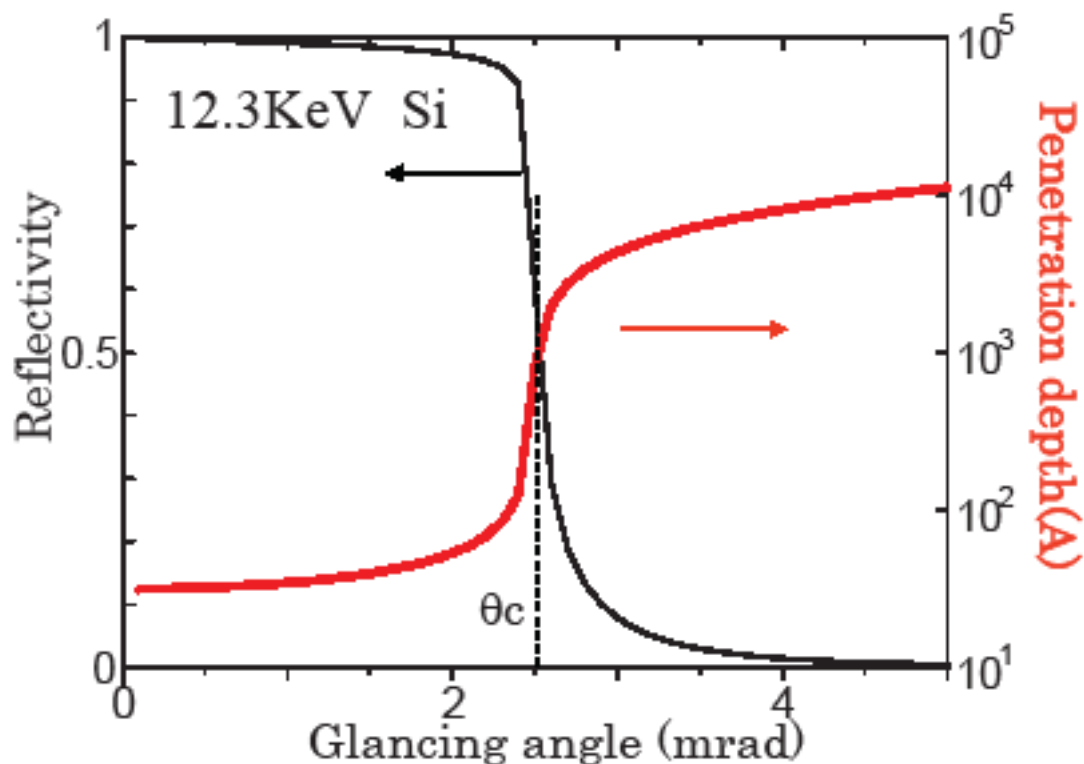
WDX

Total reflection

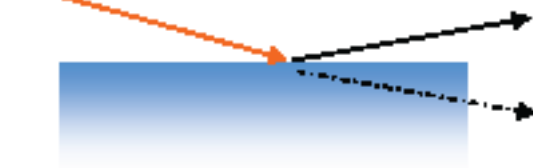


# Wavelength Dispersive Technique

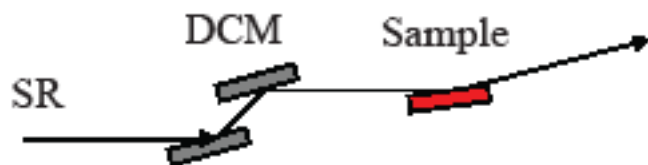




Extremely Shallow Penetration Depth



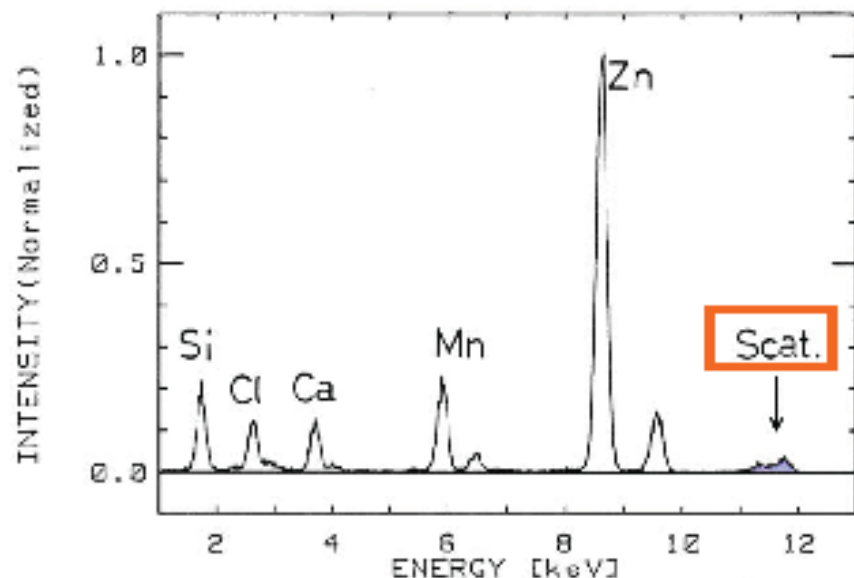
Total Reflection of X-rays at a flat and smooth surface (Si wafer, optical flat .....



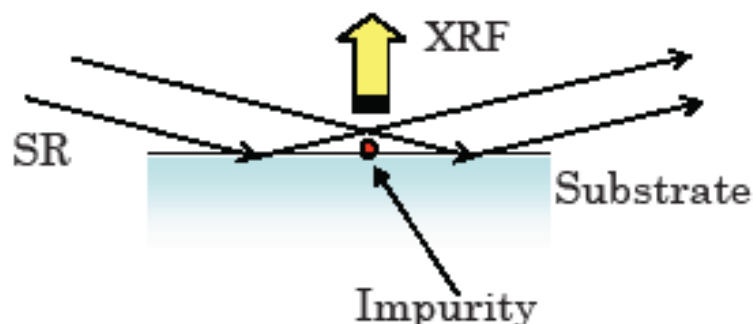
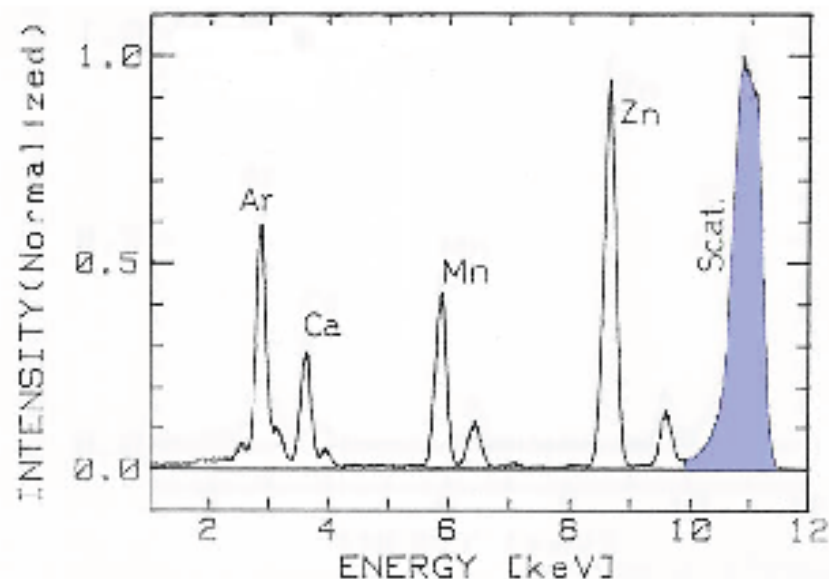


# Total-Reflection X-ray fluorescence analysis Ultra trace element analysis (TXRF)

TXRF



Conventional



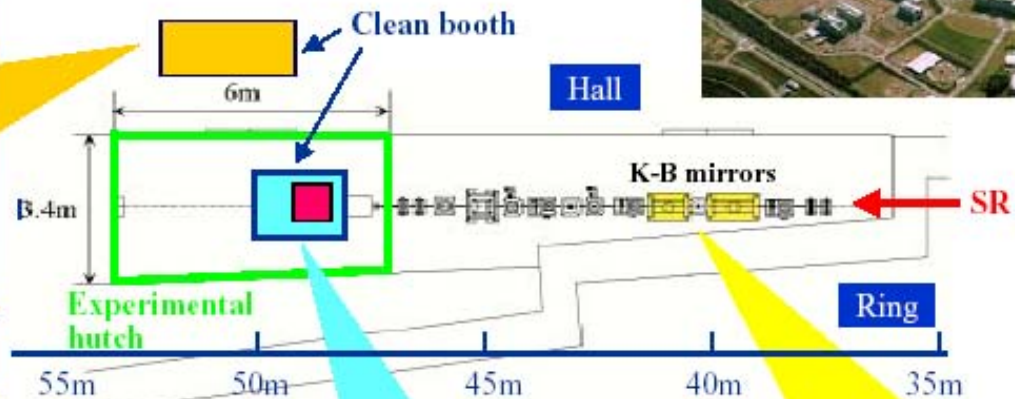
Si wafer

$10^{15}$  atoms/cm<sup>2</sup>  $\Rightarrow$   $10^8$  atoms/cm<sup>2</sup>

# TXRF Experiments at Beamline 40XU, SPring-8



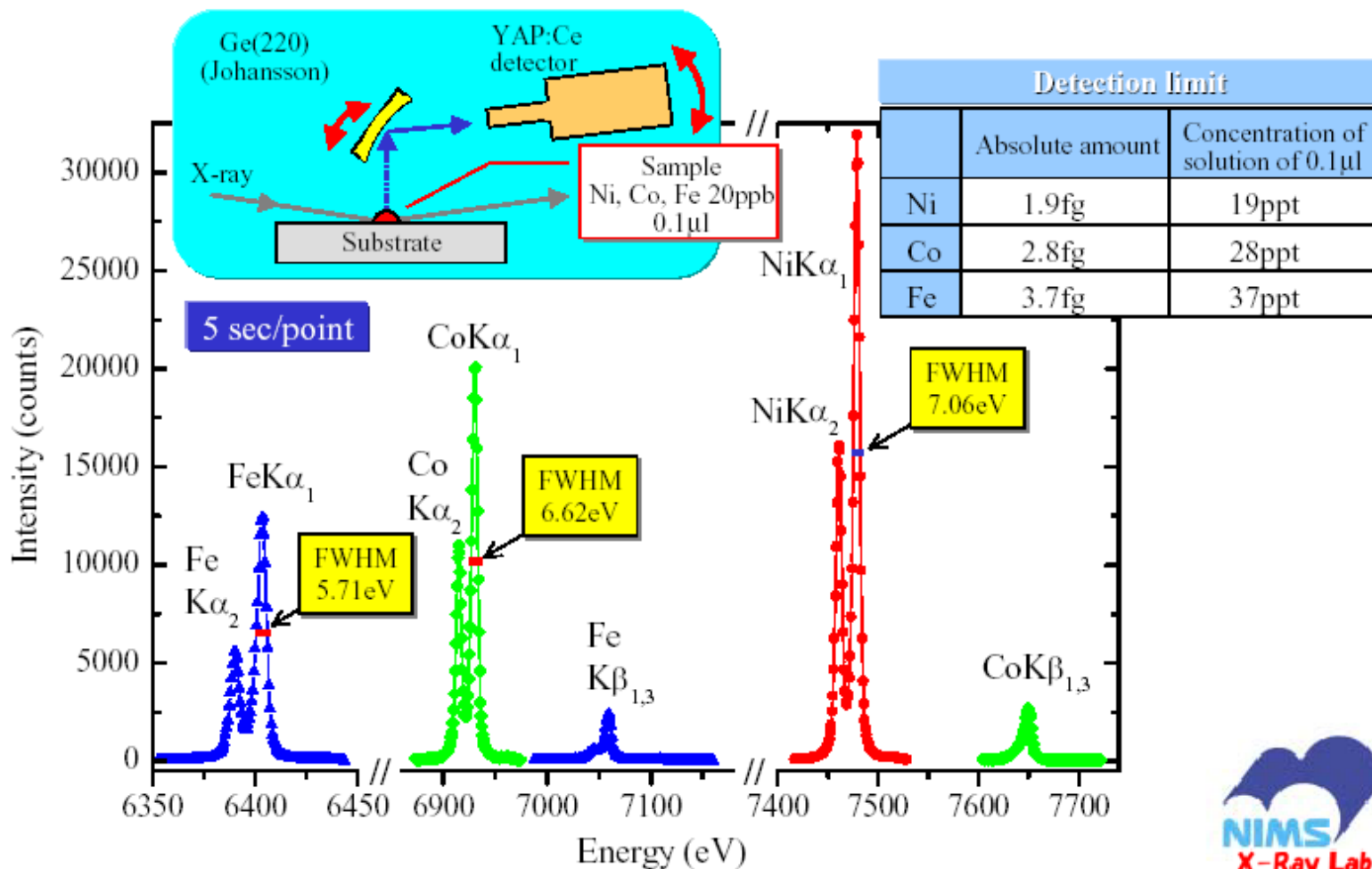
Outside the experimental hatch



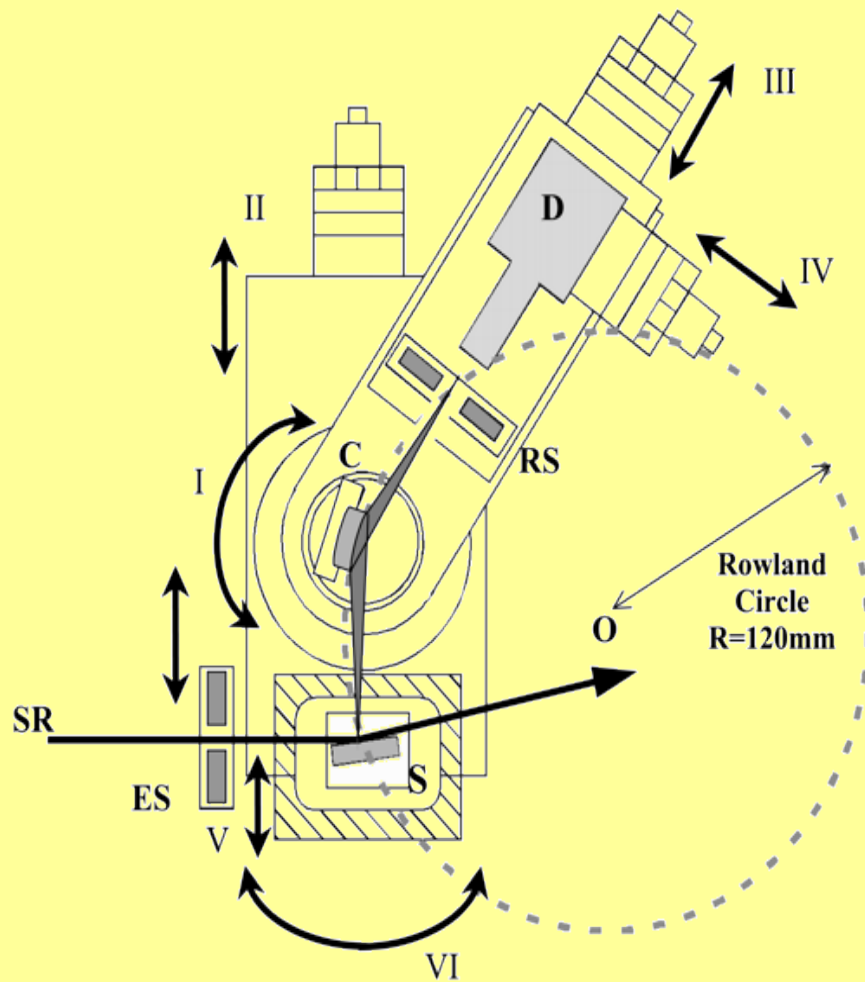
Inside the experimental hatch



# WD-TXRF Spectra for Trace Elements in Micro Drop

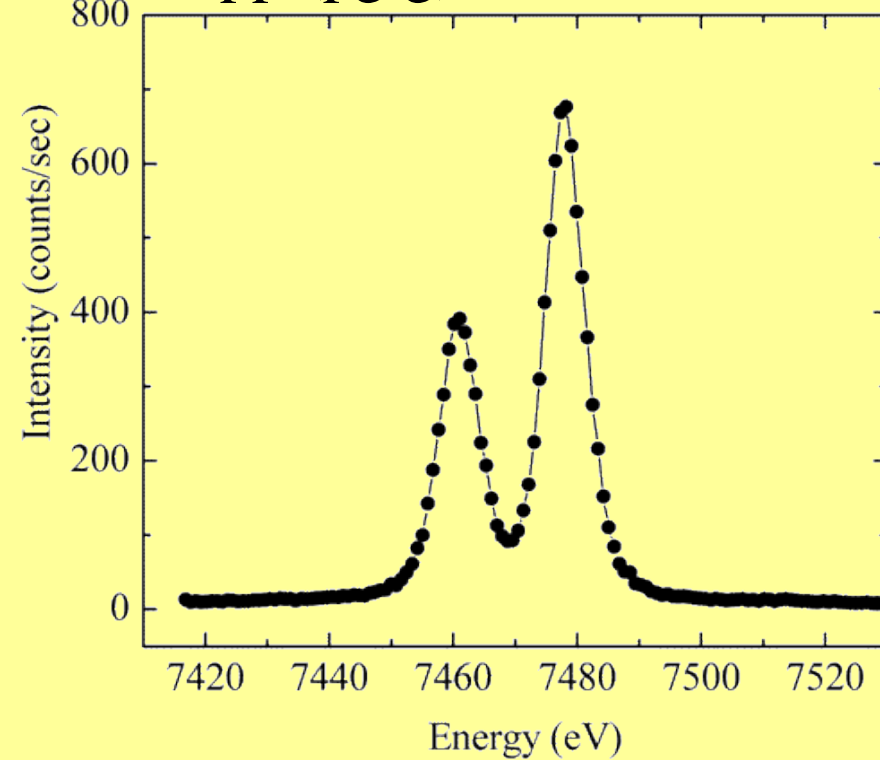


# World record of MDL by total reflection SR-XRF



$$3.1 \times 10^{-16} \text{g} = 0.31 \text{fg}$$

$$3.1 \text{ppt} (\text{pg/g}) \quad 3 \times 10^6 \text{atom}$$



(a) Crystal monochromator

C: Ge(220) Johansson type

D: YAP:Ce scintillation counter

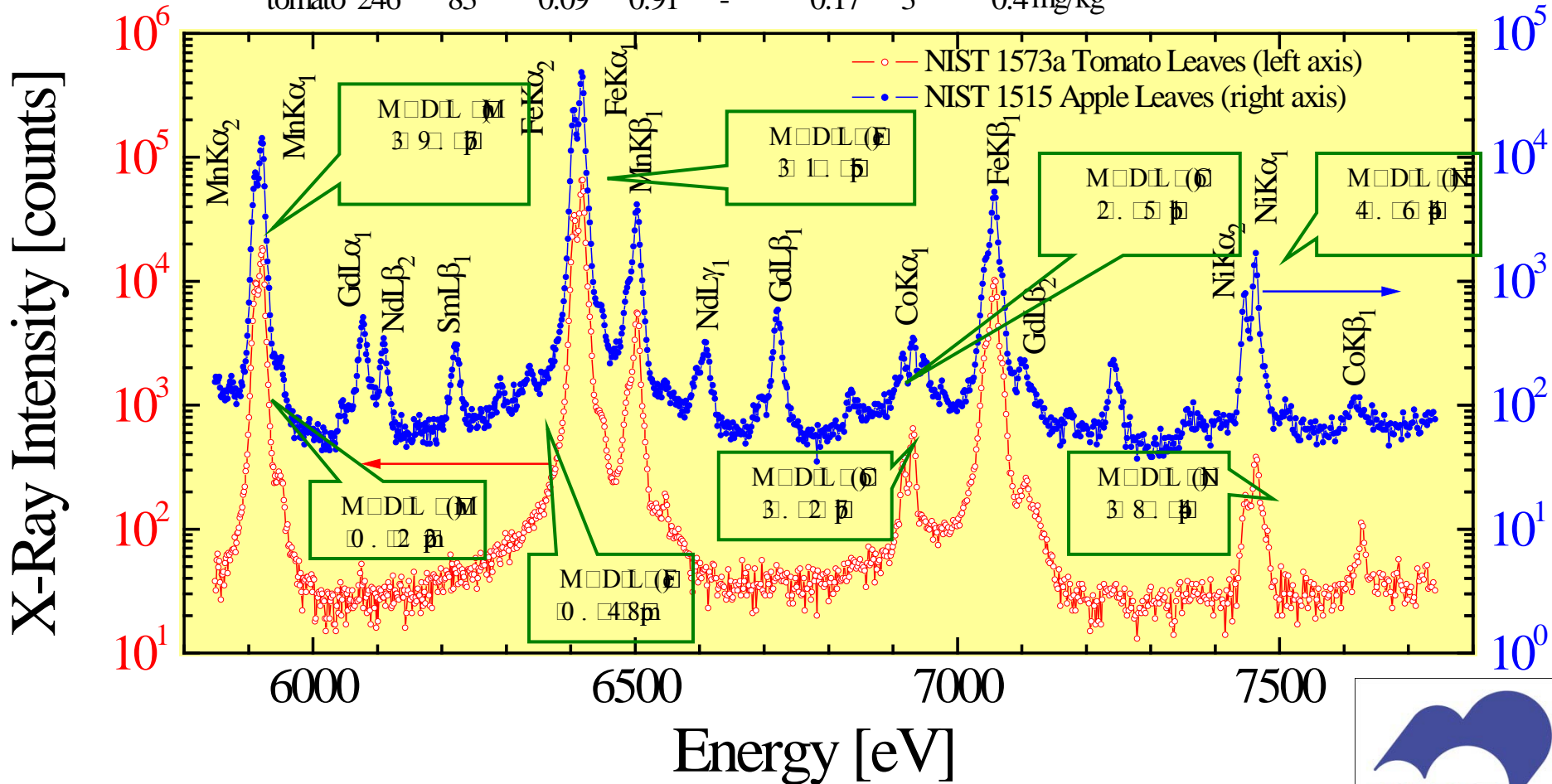
(b) XRF spectrum of 0.1 ml Ni (1 ng/g) solution (20 s/point)



# Typical XRF Spectra Obtained by R=100 Spectrometer Trace Metals in Apple and Tomato Leaves (NIST1573a and 1515)

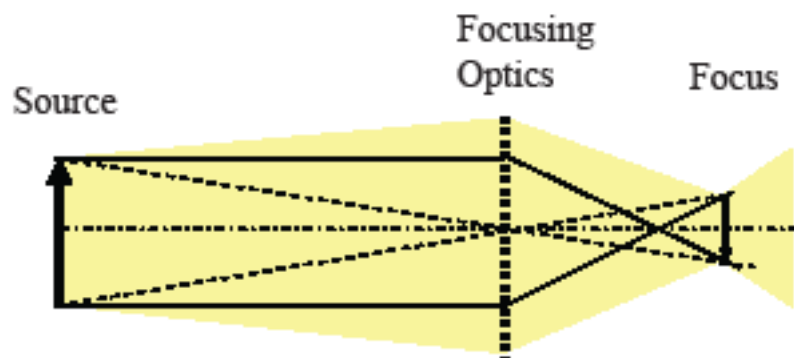
	Mn	Fe	Co	Ni	Nd	Gd	Sm	Tb
apple	54	83	0.09	0.91	17	3	3	0.4 µg/g
tomato	246	83	0.09	0.91	-	0.17	3	0.4 mg/kg

□ s □ e □ c □ / □ p



(2) Parallel beam with small  
divergence

# X-ray source and X-ray microbeam



$$1/a + 1/b = 1/f \quad M=b/a$$

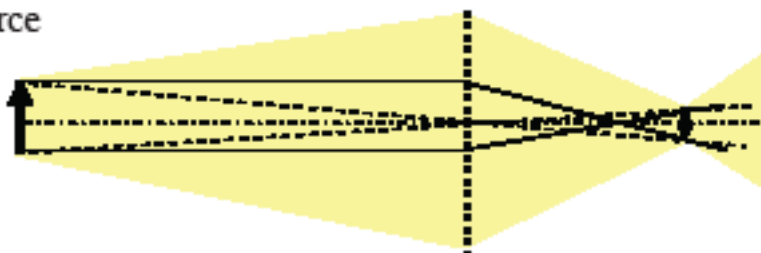
Helmholtz invariant

$$y \times u = y' \times u'$$

$y, y'$  source and focus size

$u, u'$  divergence and convergence angle

Low emittance source



Low emittance source  $\Rightarrow$  small  $y \times u$

Small source size and low divergence  
(3rd generation ring)

$\Rightarrow$  Smaller focus with higher intensity

$\Rightarrow$  micro-beam to nano-beam



# X-ray Focusing Elements

$$n = 1 - \delta - i\beta \quad \delta \sim 10^{-5}$$

X-rays: electromagnetic wave with short wavelength

## Reflection

No chromatic  
aberration

Grazing incidence mirror

spherical / aspherical  
toroidal (bent cylinder)  
elliptical, ellipsoidal  
parabolic, paraboloidal

Capillary (single, poly)

## Diffraction

Energy  
dependence

Fresnel Zone plate

Bragg-Fresnel lens

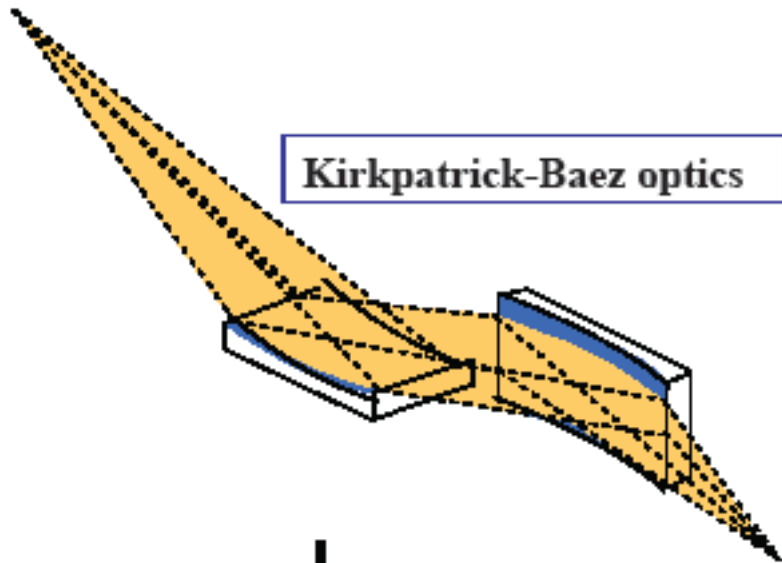
Crystal (asymmetric reflection / bent crystal)

## Refraction

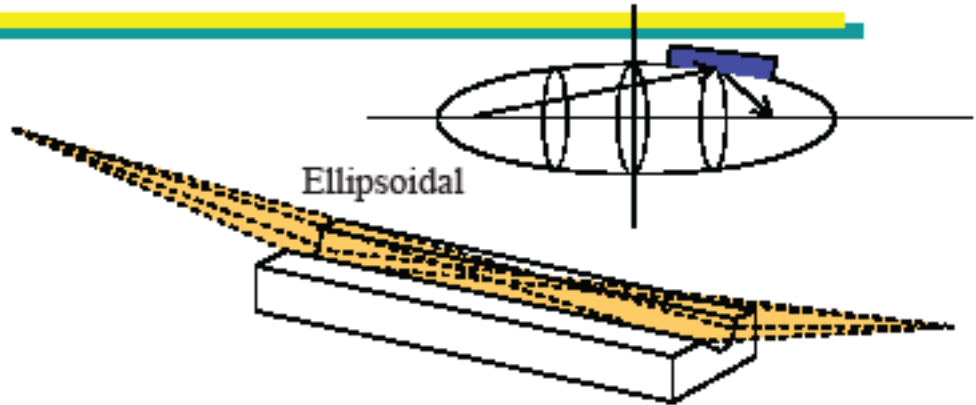
Compound refractive lens

# X-ray microbeam Optics

Kirkpatrick-Baez optics



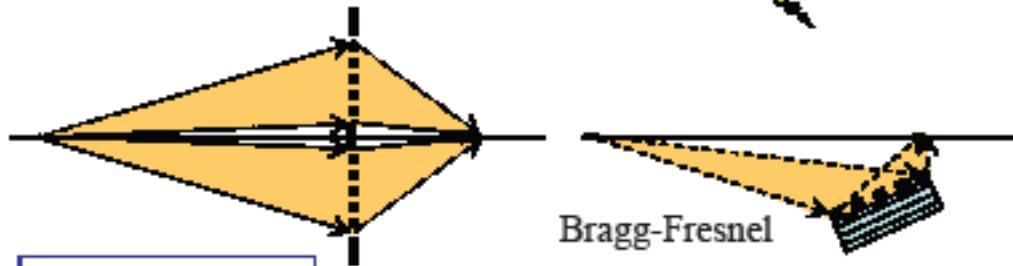
Ellipsoidal



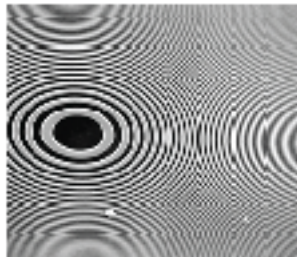
Single tapered capillary



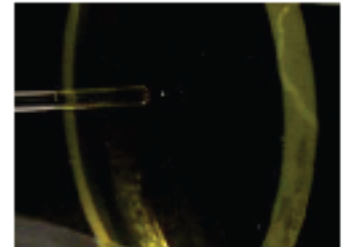
Bragg-Fresnel



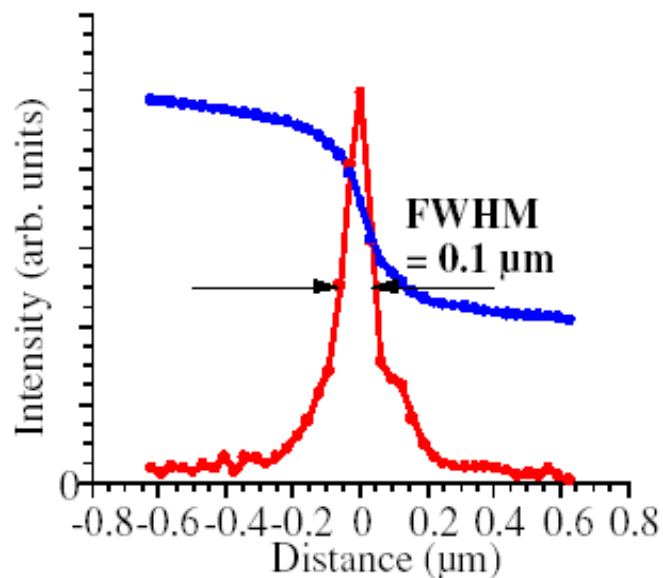
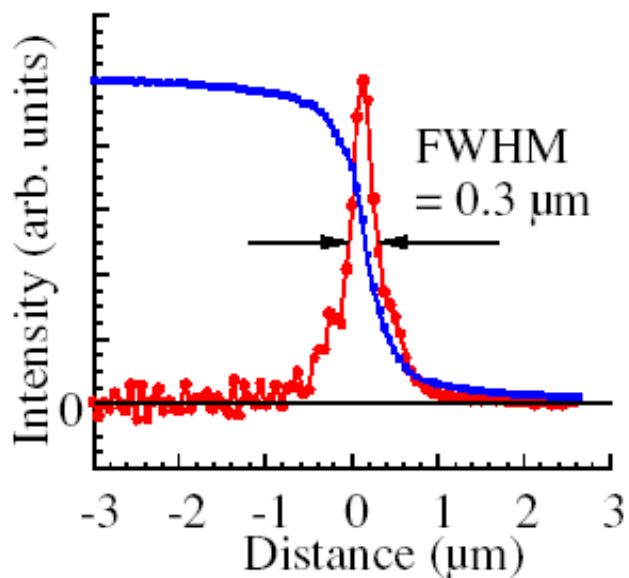
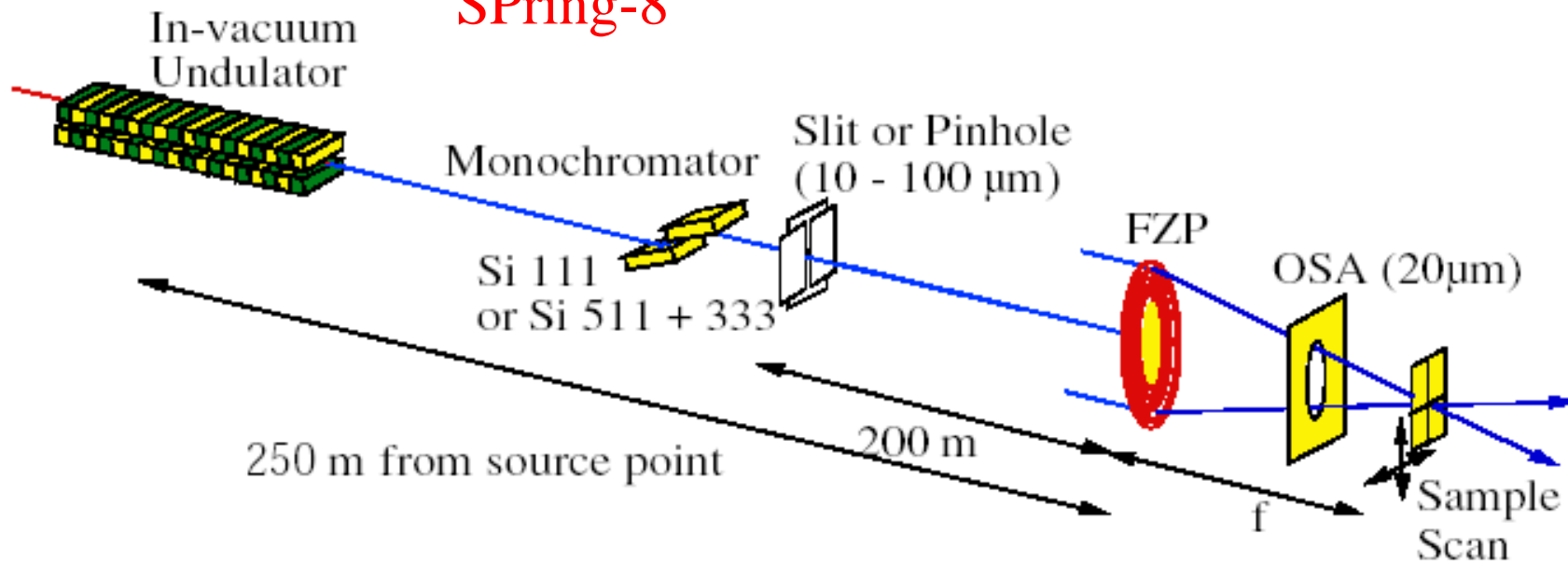
Fresnel zone optics



Compound refractive optics



# SPring-8



Beam profile at focal points made by FZP at 8keV

# **Application of SR-XRF to in vivo analysis of biological sample**

**Study of hyper-accumulator plants of As and Cd**



# Phytoremediation

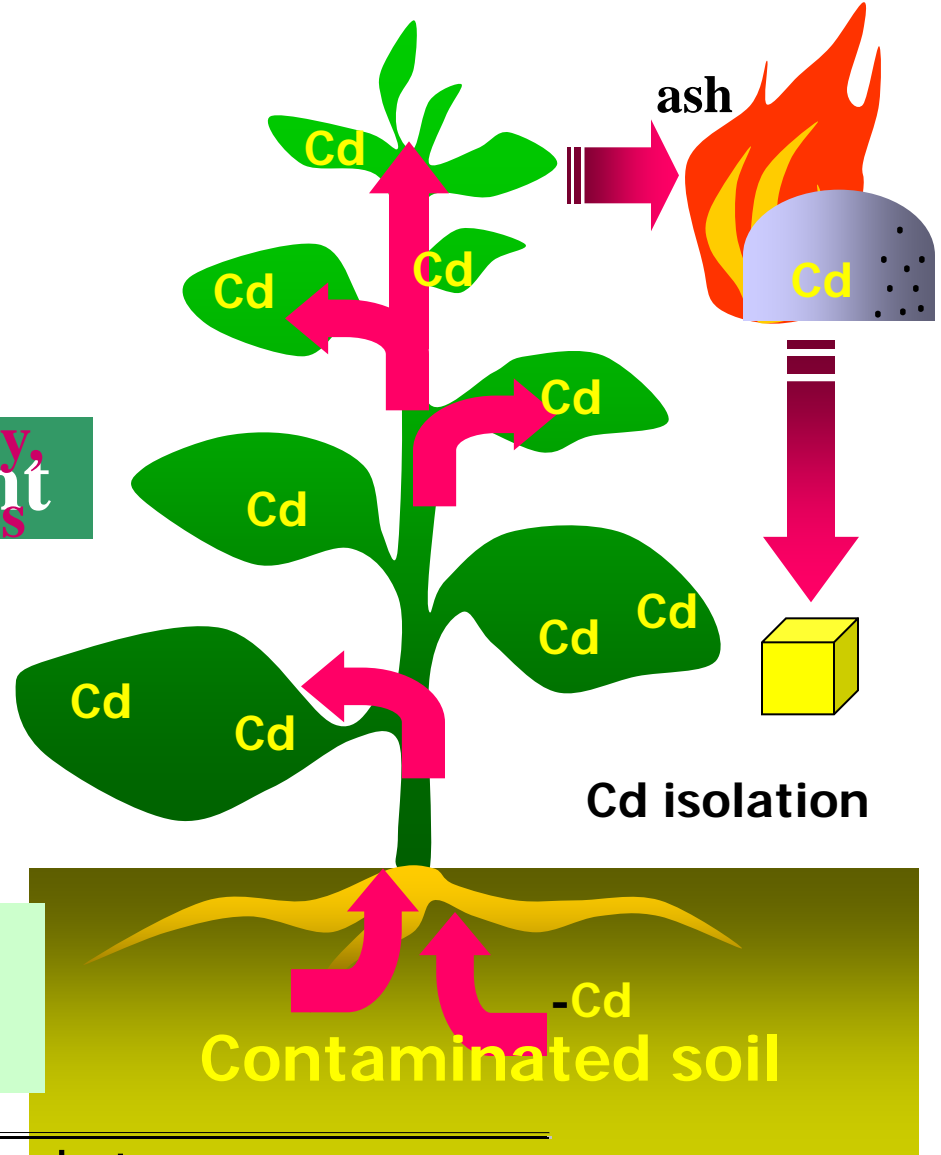


plant



remediate

Phytoremediation is a technology that uses plants to remove, destroy, or sequester hazardous substances from the environment.  
**Merit:** no damage, low cost, preservation of surface, etc...



Some specific kinds of plants are known to be heavy metal hyperaccumulator

Element	conc./ ppm	plant
As <sup>*1</sup>	22,630	<i>Pteris vittata</i> L. (モエジマシダ)
Cd	11,000	<i>Athyrium yokoscense</i> (ヘビノネゴザ)
Pb	34,500	<i>Brassica juncea</i> (カラシナ)

\*1 L. Q. Ma, et al., *Nature*, (2001), 409, 579.



# Phytoremediation

Environmentally friendly low cost  
technique

Key: Use of hyperaccumulator plant

As



Arsenic Hyperaccumulator  
*Pteris vittata* L.  
(モエジマシダ)

Cd



Cd Hyperaccumulator  
*Arabidopsis halleri* ssp. *gemmifera*  
(ハクサンハタザオ)



300kg (fresh weight)

≡ 270g As



**Application Example**  
**Chinese brake fern (*Pteris vittata* L.)**

Application example 2: Cd hyper-accumulating plant, *Arabidopsis halleri* ssp. *Gemmifer*

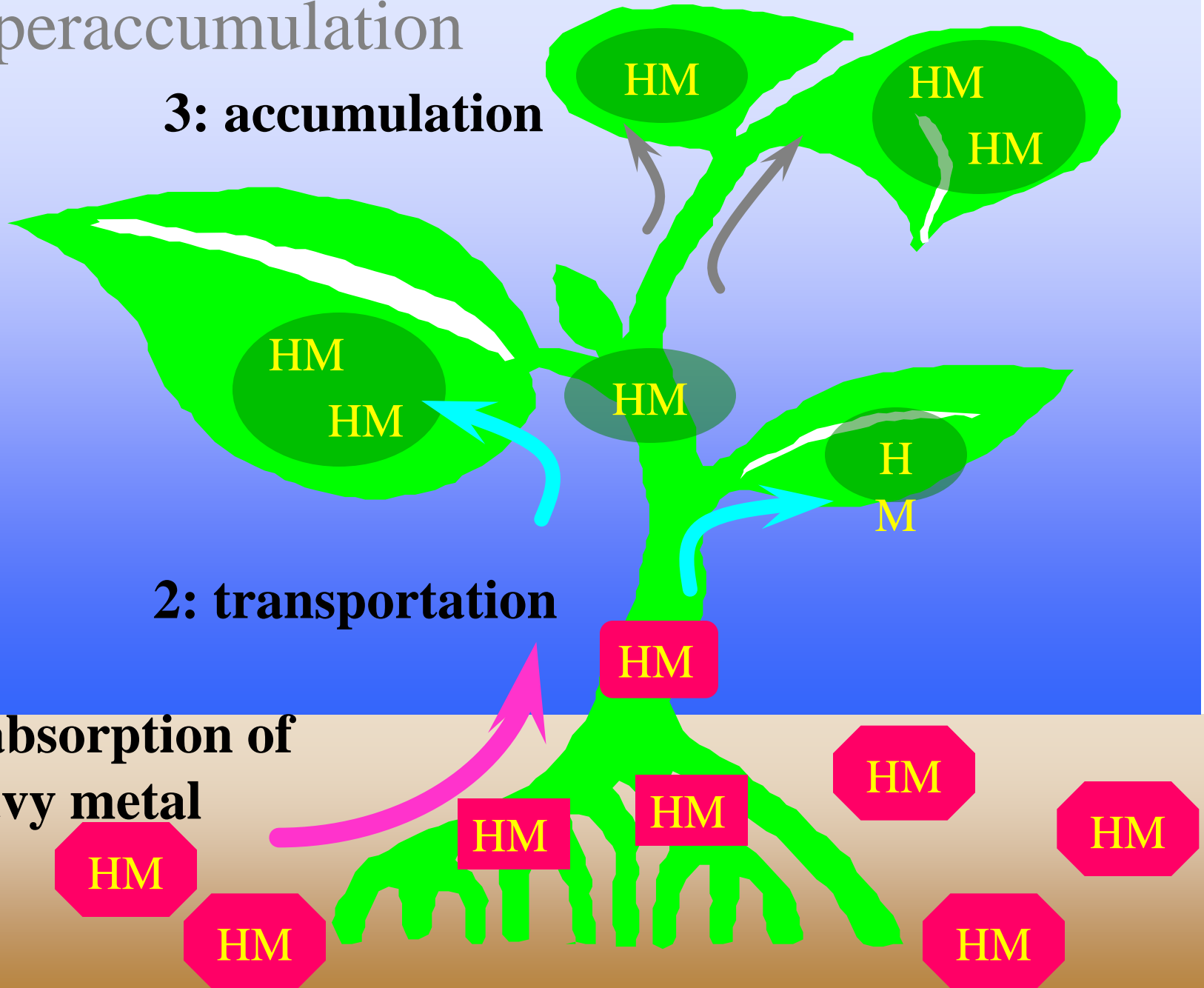


# Hyperaccumulation

**3: accumulation**

**2: transportation**

**1: absorption of heavy metal**



# Application of SR X-ray analyses

**Two dimensional multi-element  
nondestructive analysis in cell level**

**→  $\mu$ -XRF imaging**

**▪ In vivo chemical state analysis of metals in  
the plant**

**→ X-ray absorption fine structure (XAFS)  
analysis**

**▪ Chemical state analysis in cell level**

**→  $\mu$ -XANES**

# As hyperaccumulator

Chinese brake fern (*Pteris vittata* L.)

(As: *ca.* 22,000  $\mu\text{g}$  /g dry weight)

**Arsenic distribution and speciation in an arsenic hyperaccumulator fern by X-ray spectrometry utilizing a synchrotron radiation source**

**A. Hokura, R. Onuma, Y. Terada, N. Kitajima, T. Abe, H. Saito, S. Yoshida and I. Nakai**

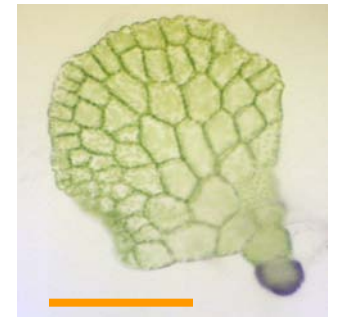
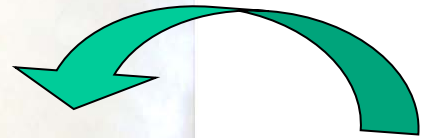
**Journal of Analytical Atomic Spectrometry, 21, 321-328 (2006)**

# Life of fern

*Pteris vittata* L.

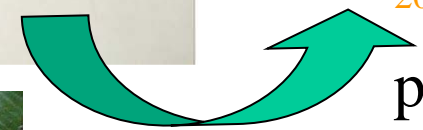


fertilized

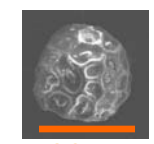


200 μm

prothallium



Fertile pinna



30 μm  
spore

frond

# Cultivation of fern



arsenic-contaminated soil

As level in soil :  $481 \mu\text{g g}^{-1}\text{dry}$

Term :  $\sim 3$  weeks

Average As level :  $\sim 720 \mu\text{g /g dry}$



culture medium containing As  
(1 ppm 4days)

As level\*

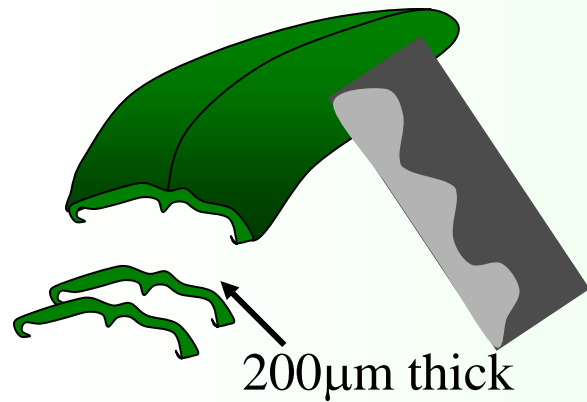
pinna :  $2800 - 4500 \mu\text{g g}^{-1}\text{dry}$

midrib of a frond :  $84 - 250 \mu\text{g /g dry}$

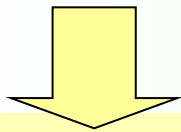
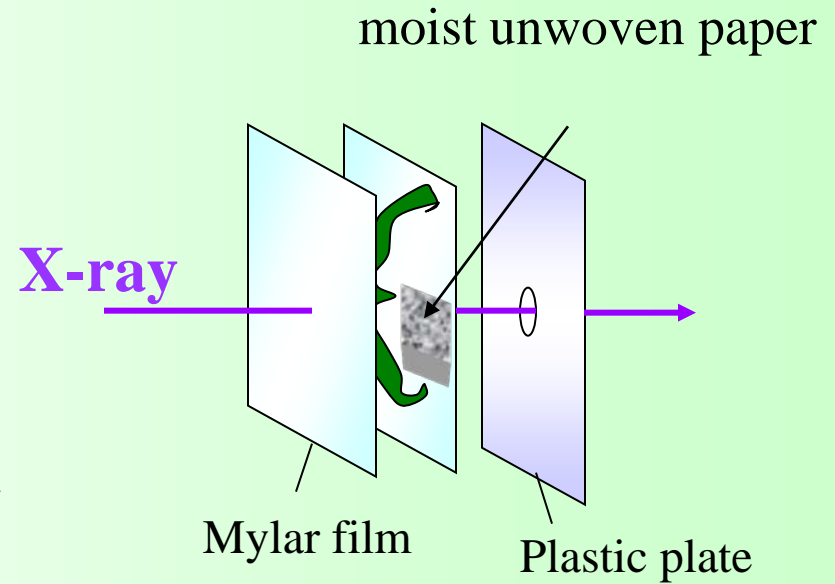
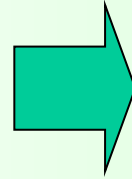
\* Anal. By AAS



# Sample preparation for microbeam analysis



vertical slicer (Model HS-1, JASCO Co.)



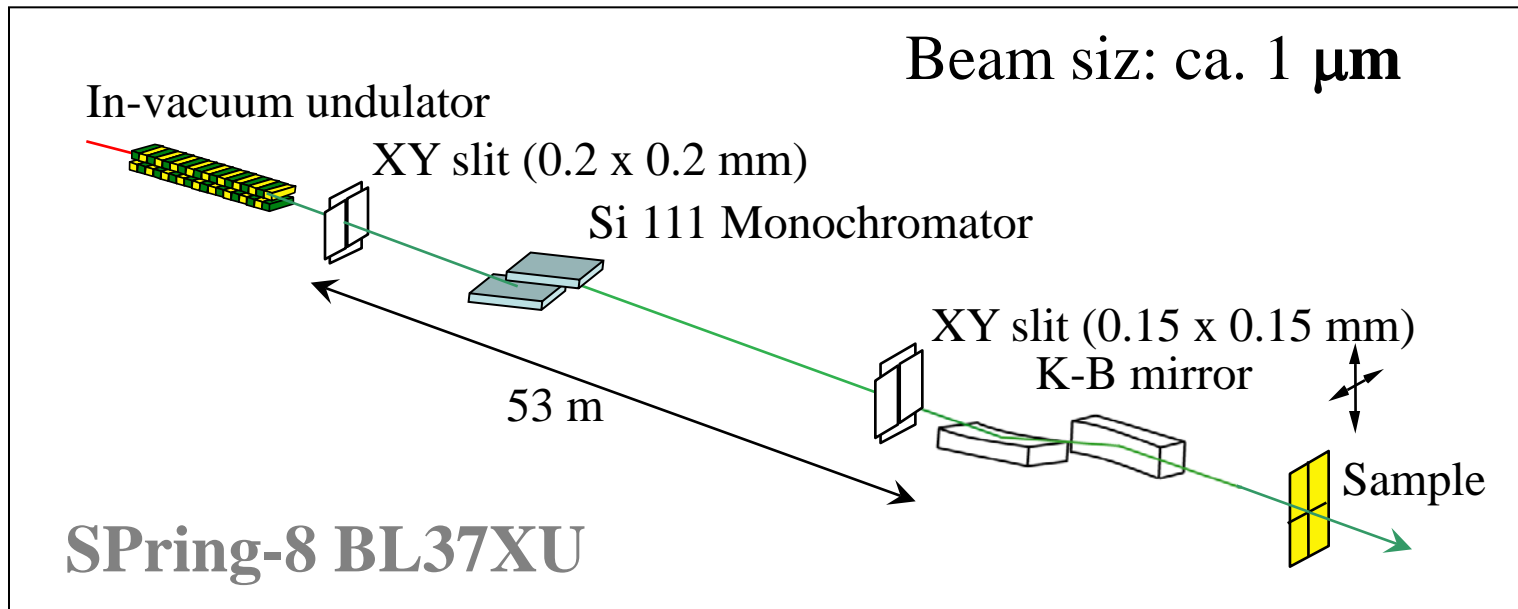
freeze dry of frozen

# $\mu$ -XRF, $\mu$ -XANES

X-ray energy

As: 12.8keV

Cd: 37.0keV

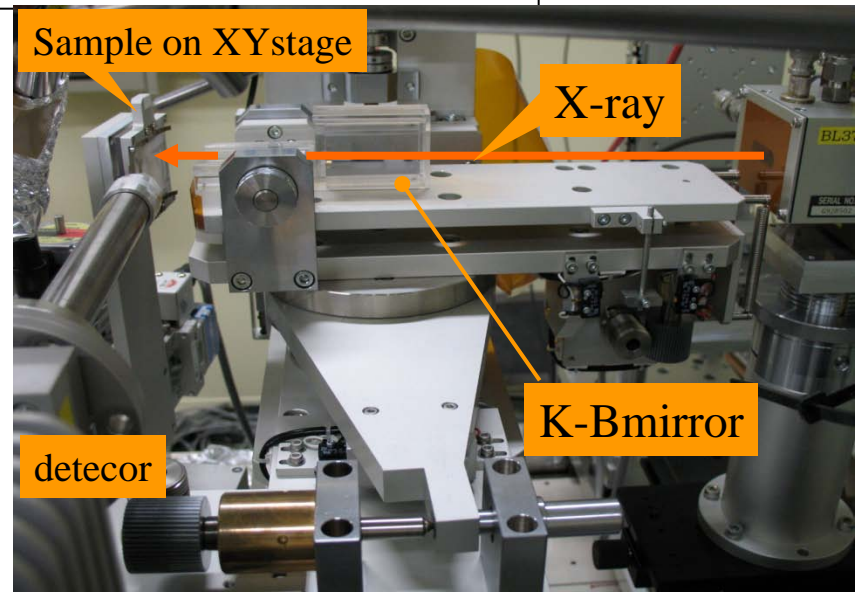


## - BEAMLINE DESCRIPTION -

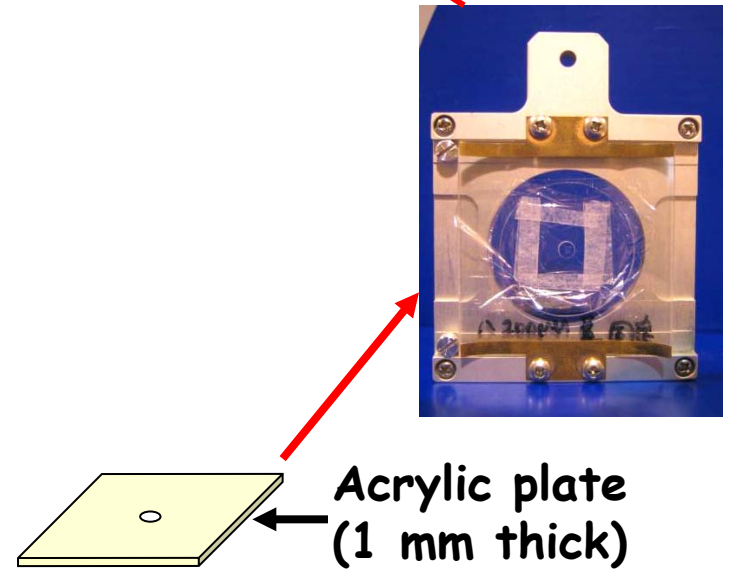
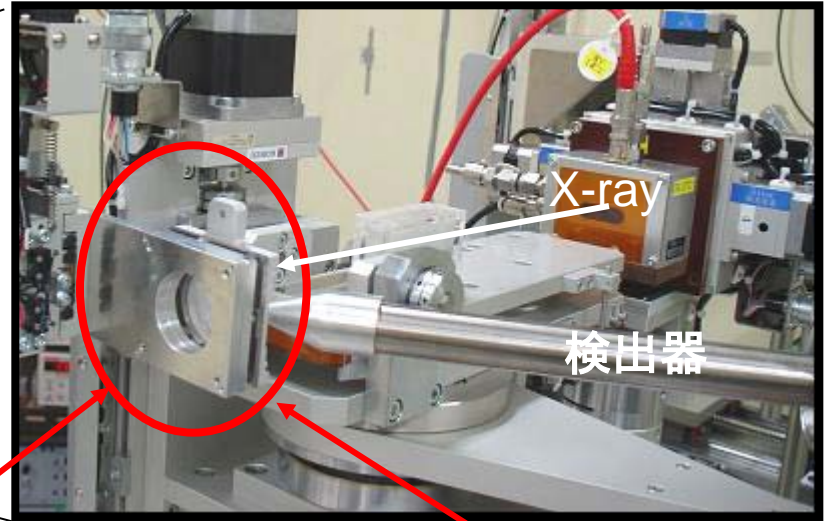
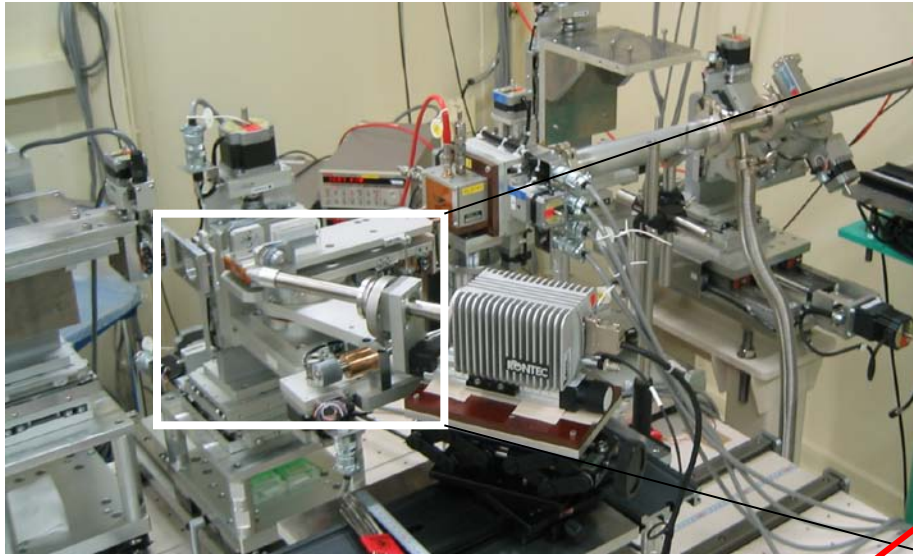
The light source : In-vacuum type undulator  
 (Period length : 32 mm, the number of period : 140)  
 Monochromator : Double-crystal monochromator  
 located 43 m from the source

Table Details of focusing optics by K-B mirror

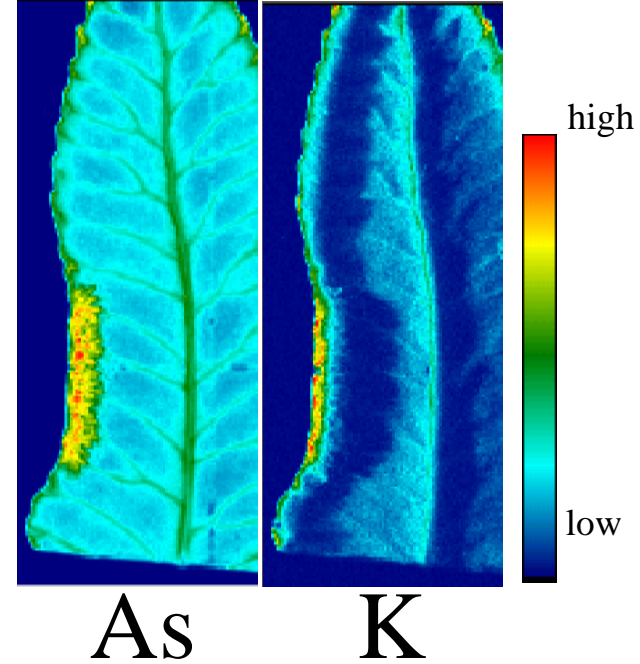
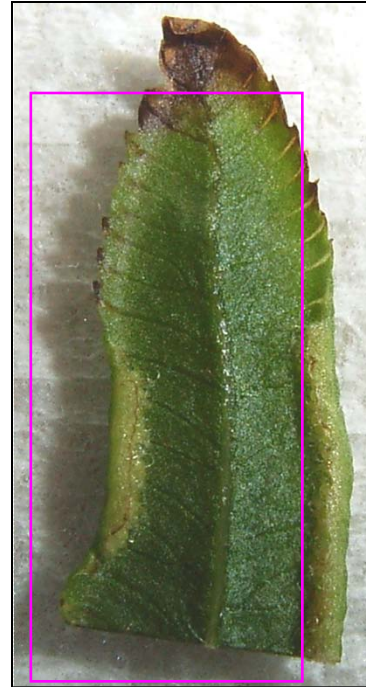
	37 keV <sup>[1]</sup>	12.8 keV
Material	fused quartz	fused quartz
Surface	platinum coated	platinum coated
Focal length (1 <sup>st</sup> mirror)	250 mm	100 mm
(2 <sup>nd</sup> mirror)	100 mm	50 mm
Average glancing angle	0.8 mrad	2.8 mrad



# Instrument ~Spring-8 BL37XU~



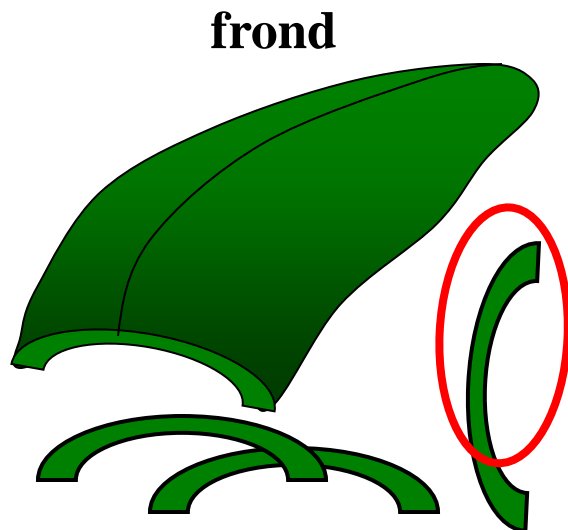
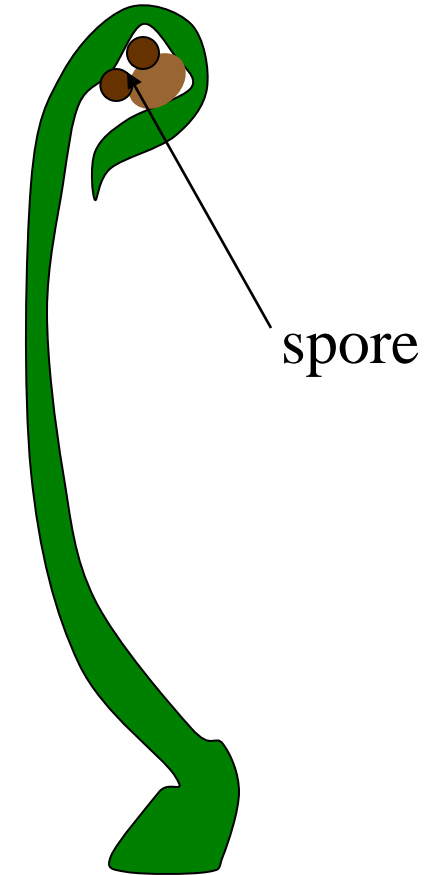
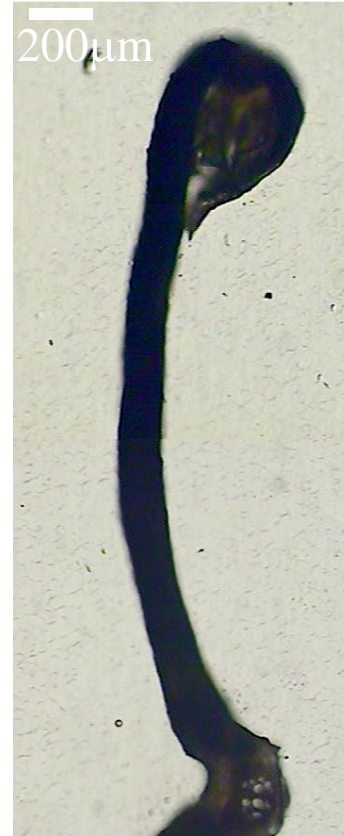
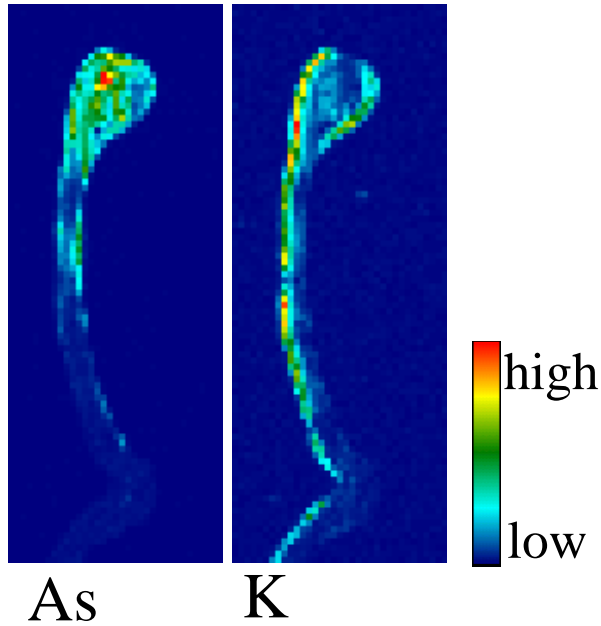
# XRF imaging for As, K, and Ca of pinnae



Accumulation of As at Fertile with spores along marginal parts

high  
low

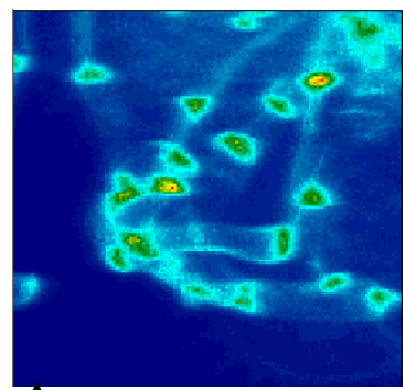
# A section of pinna



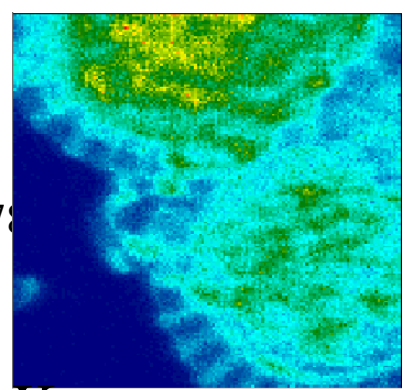
X-ray Energy : **14.999 keV**  
Beam size : **50 μm × 50 μm**  
Step number : **35 point × 90 point**  
measurement time : **1 sec/point**

X-ray Energy : 12.8 keV  
Beam size : 1.5  $\mu\text{m}$   $\times$  1.5  $\mu\text{m}$   
Exposure time : 0.2 sec. / point  
Point : 150 point  $\times$  150 point

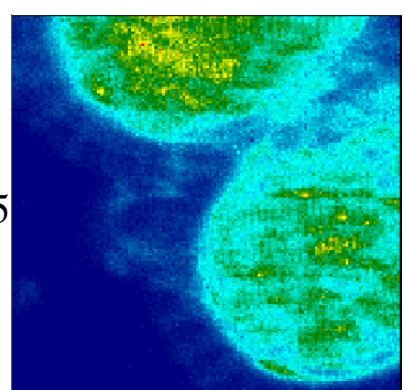
# M-XRF imaging at Spring-8



As



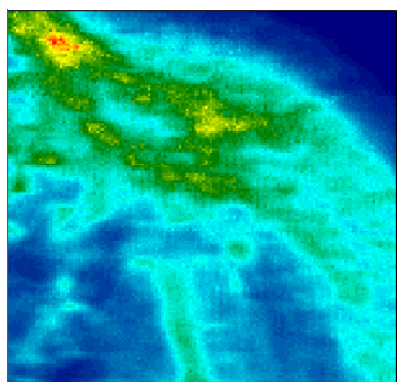
K



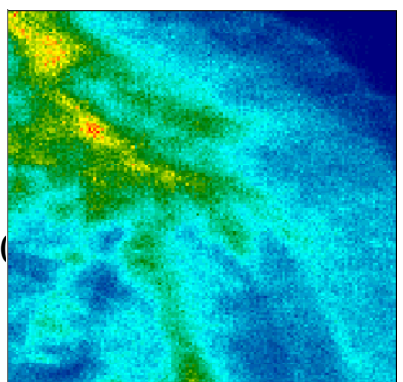
Ca

X-ray Energy : 12.8 keV  
Beam size : 1.5  $\mu\text{m}$   $\times$  1.5  $\mu\text{m}$   
Exposure time : 0.2 sec. / point  
Point : 150 point  $\times$  150 point

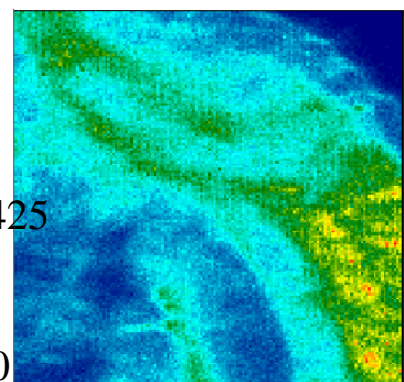
As level is low at spore



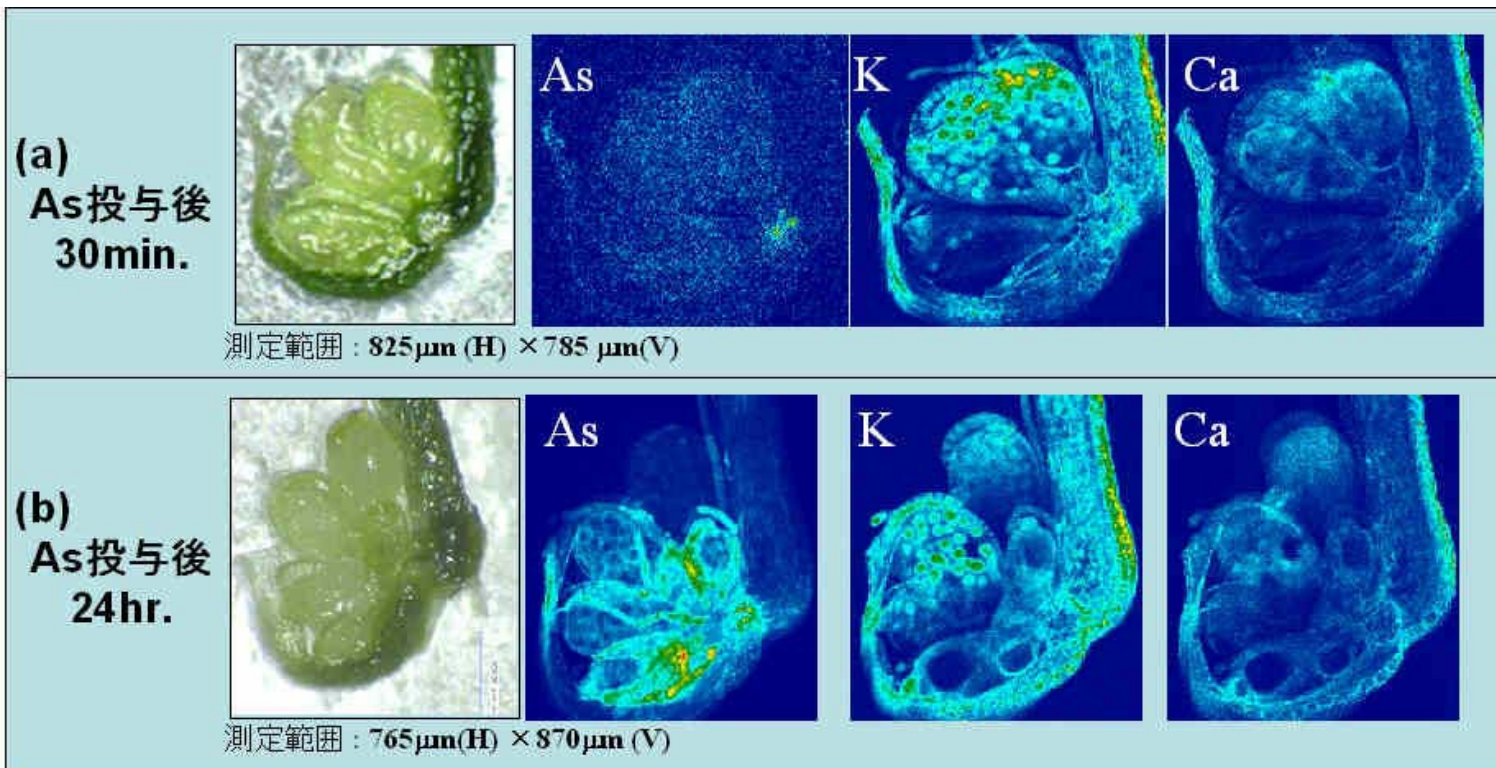
As



K



Ca



X-ray Energy : 12.8 keV

Beam size : 1.6  $\mu$ m  $\times$  2.3  $\mu$ m

Step size : 5  $\mu$ m  $\times$  5  $\mu$ m

measurement time : 0.1 sec/point

Low  High  
Normalized Intensity

$\mu$ -XRF imaging of leaf at (a)30min and (b)24 hr after arsenic feeding.

Time dependent observation of arsenic transfer in leaf tissue  
of hyperaccumulator fern

(3) Energy tunability

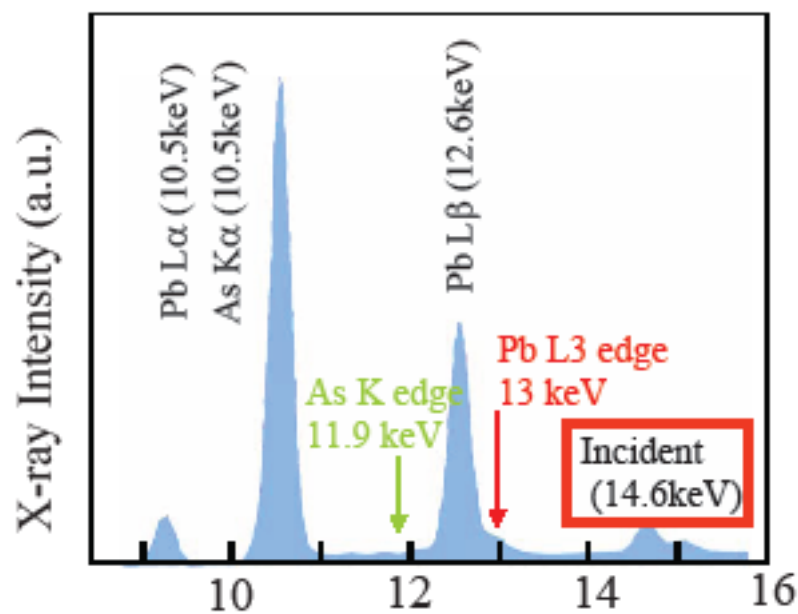
Chemical state analysis  
by Fluorescence -XAFS



# Selective Excitation :

## Resolving overlapping peaks: PbL $\alpha$ vs. As K $\alpha$ Case

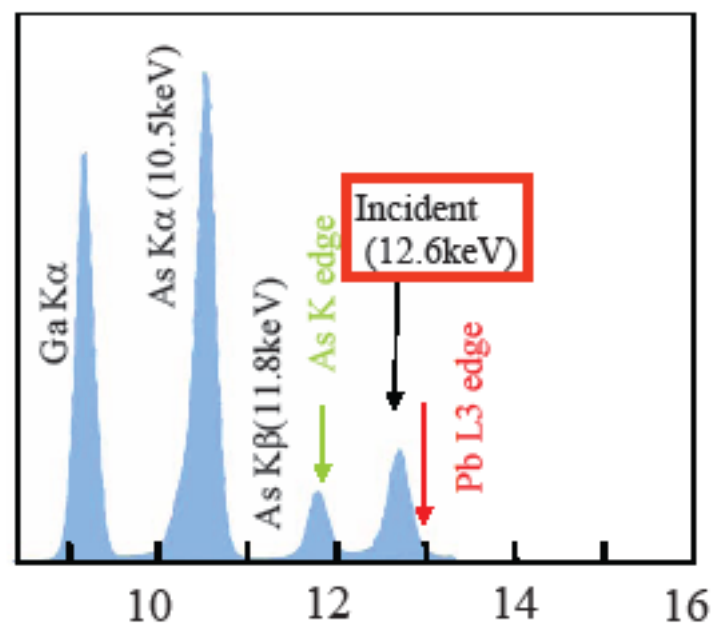
As Kedge < PbL3 edge < E<sub>0</sub>



Fluorescent X-ray Energy (keV)

Both As K and Pb L are excited.

As Kedge < E<sub>0</sub> < PbL3 edge



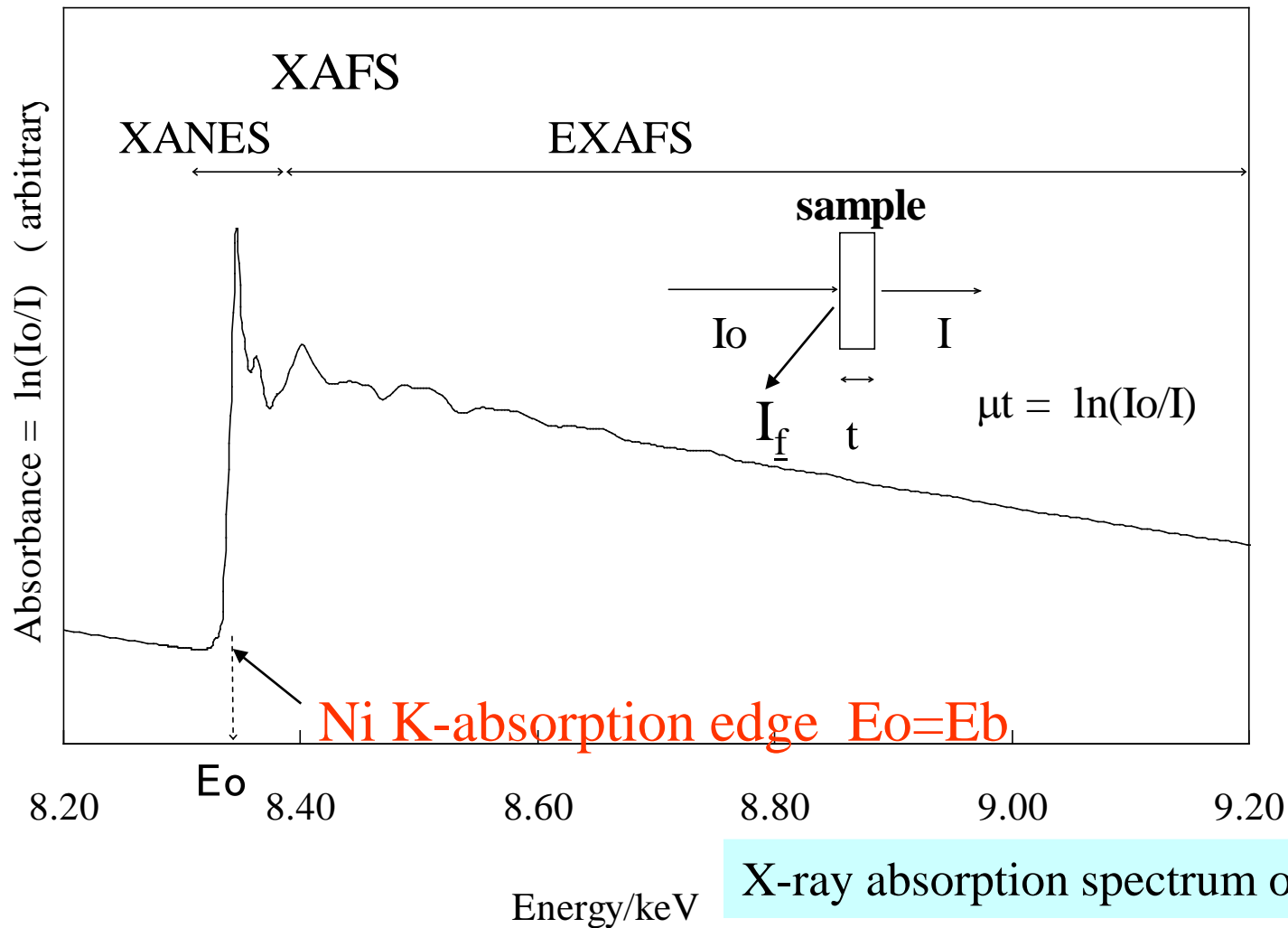
Fluorescent X-ray Energy (keV)

As K series alone is excited.  
=>As quantification becomes possible.



# Chemical State Analysis

- **XAFS (X-ray Absorption Fine Structure)**
  - **XANES**
    - Chemical shift of absorption edge
    - The intensity of the white line
  - EXAFS
    - Local structure
    - Coordination number
- **X-ray Emission**
  - Chemical state analysis
    - Chemical shift of the K or L emission lines
    - Intensity ratio of  $K\alpha$  and  $K\beta$
  - Emission Spectroscopy
    - Resonant inelastic emission spectroscopy
    - .....



X-ray absorption spectrum of  $\text{LiNiO}_2$

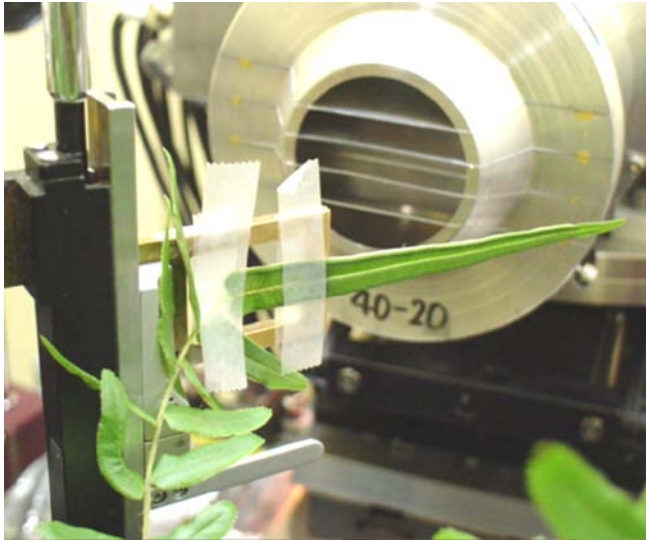
**XANES:** X-ray absorption near edge structure

electronic state, oxidation number

**EXAFS:** Extended X-ray absorption fine structure

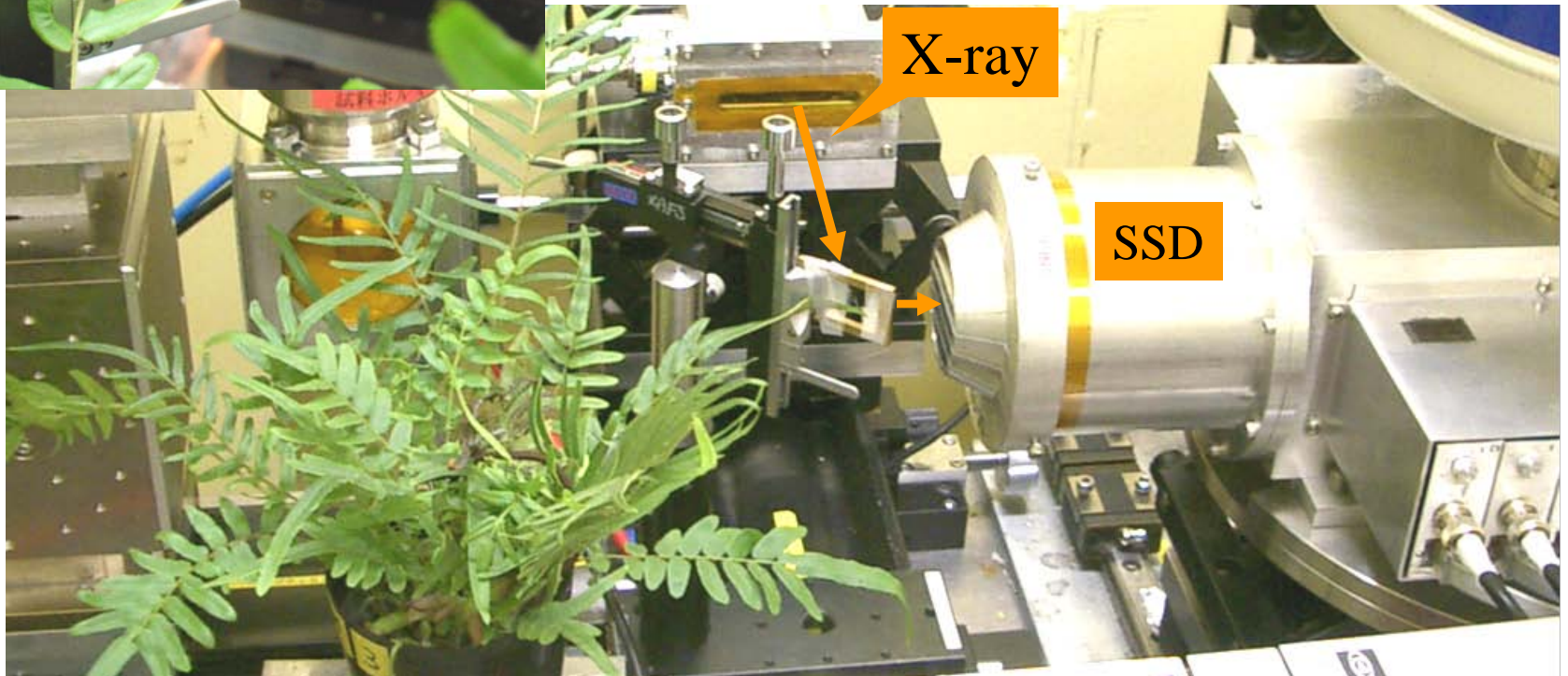
local structure (atomic distance and coordination No.)

# XAFS analysis



KEK PF BL12C  
As K-edge (11.863 keV)  
Si(111) double crystal  
Fluorescence mode  
19elements-SSD

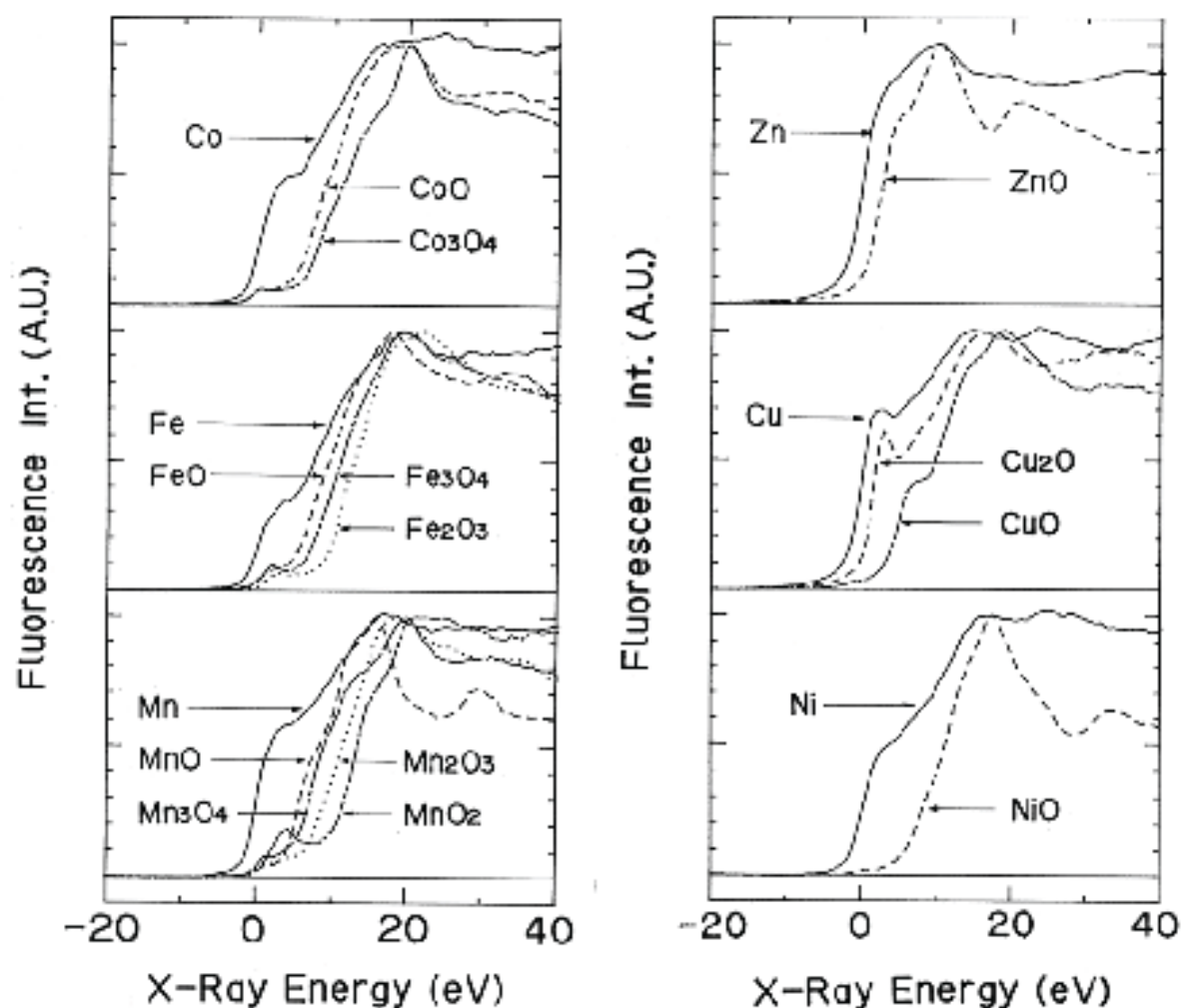
*in vivo* XAFS





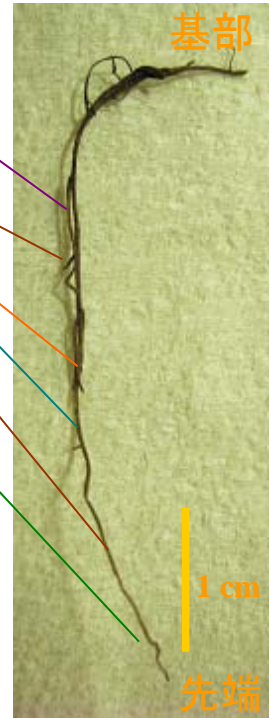
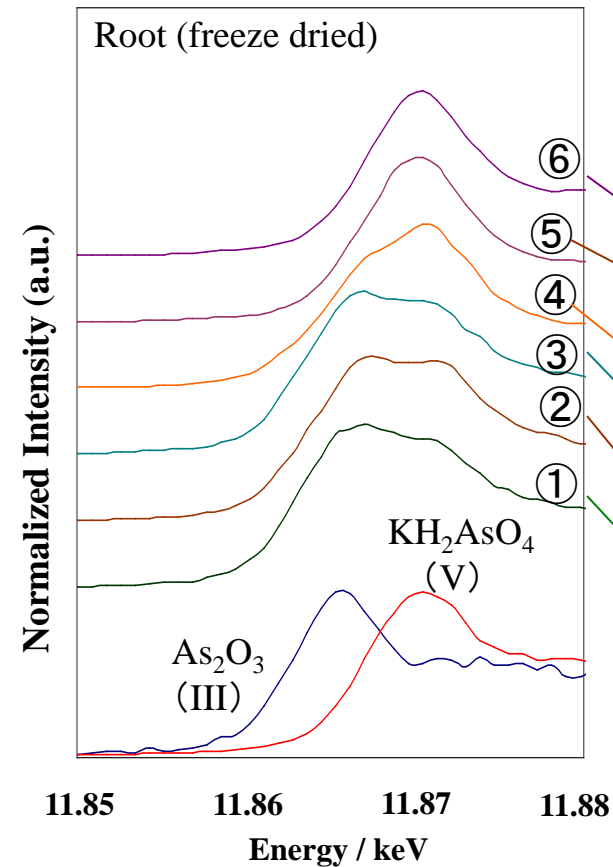
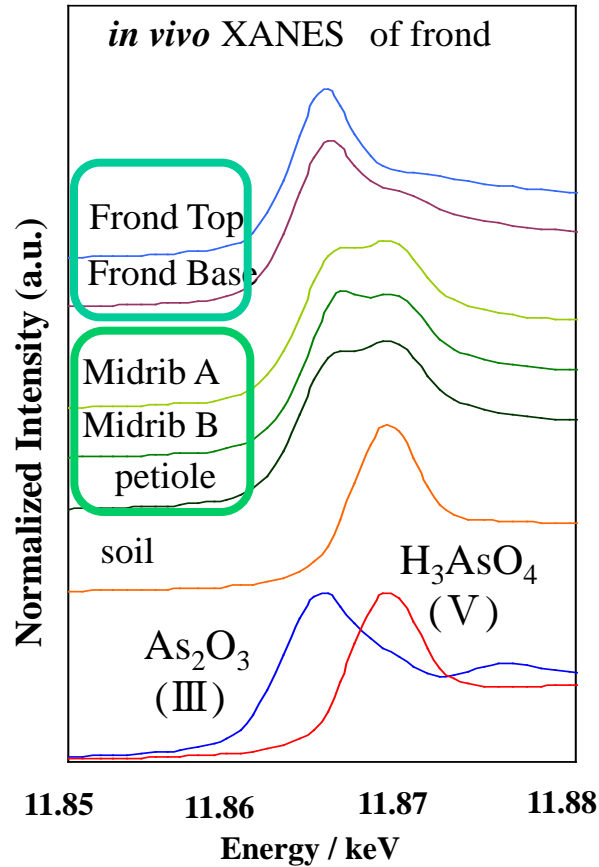
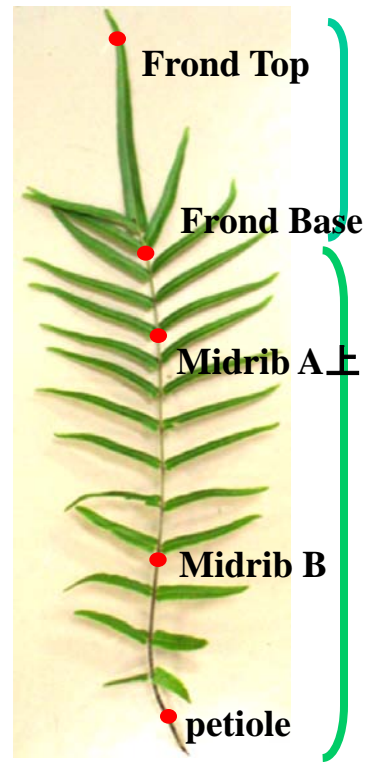
# Chemical State analysis by XANES

-Chemical Shift of X-ray Absorption edge-



Fingerprint  
Method

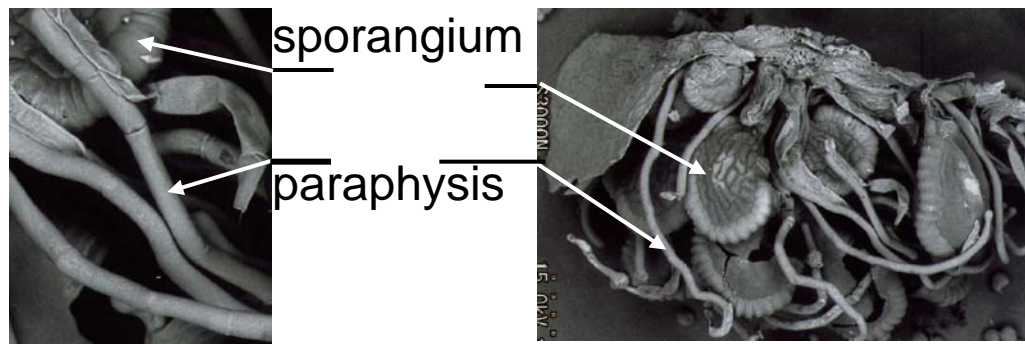
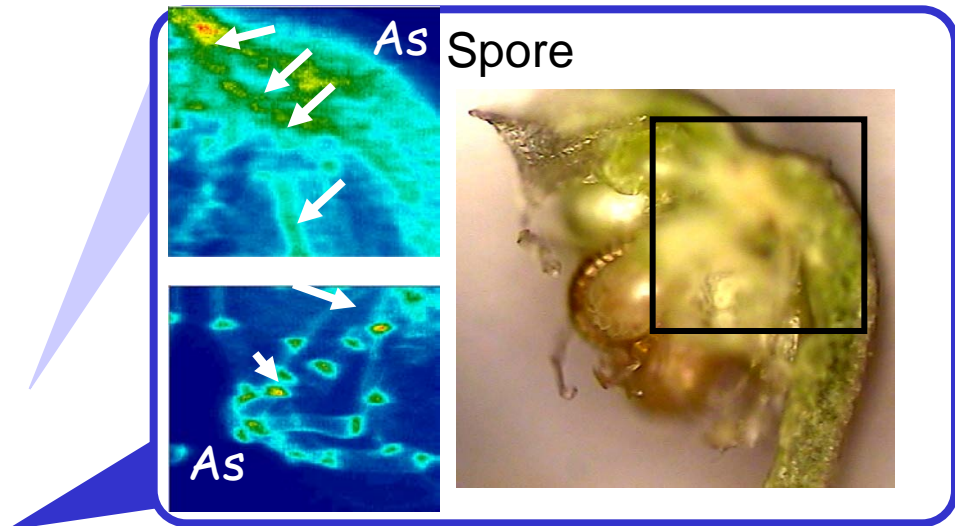
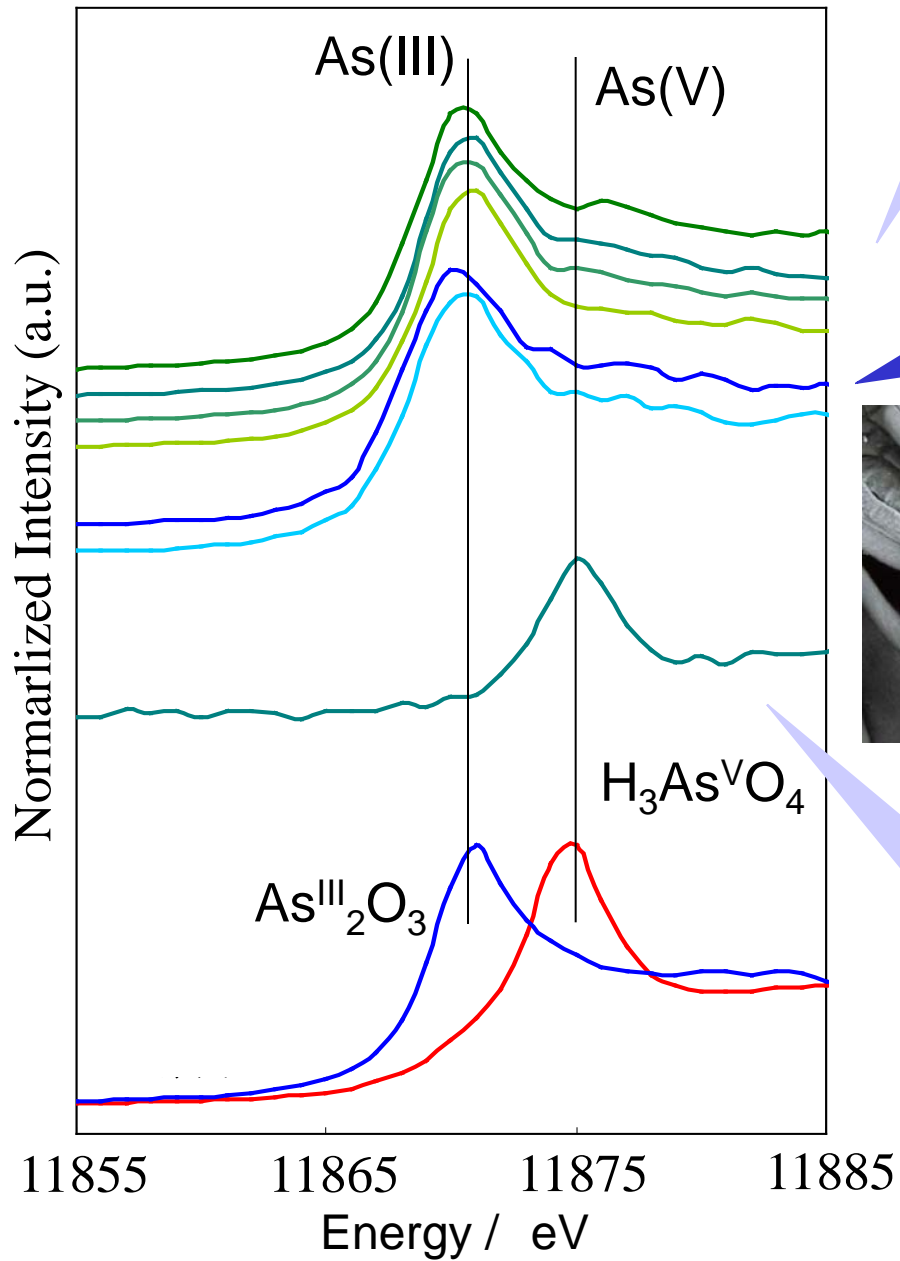
# As K-edge XANES analysis



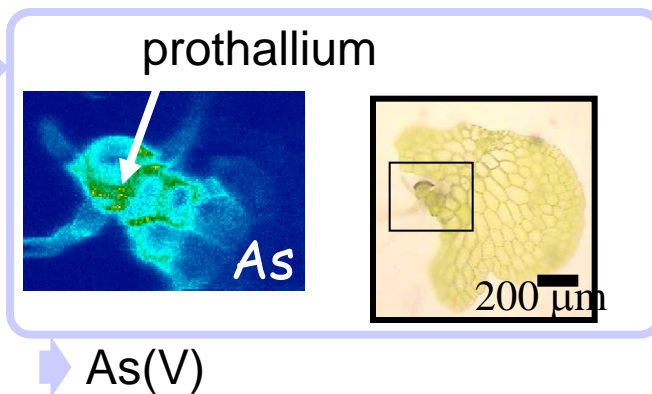
Fron  
PF BL-12C

Root

# As K-edge XANES



As exits as  $\text{As}^{3+}$



# *Arabidopsis halleri*

Cd and Zn hyper-accumulator

and

Cd in Rice

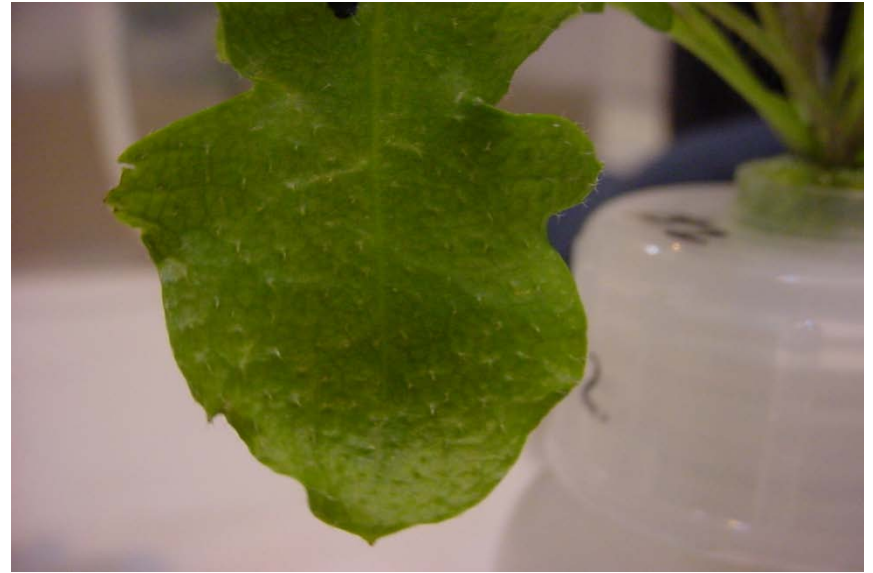
**Micro X-ray fluorescence imaging and micro X-ray absorption spectroscopy of cadmium hyper-accumulating plant, *Arabidopsis halleri* ssp. *gemmifera*, using high-energy synchrotron radiation**

***Journal of Analytical Atomic Spectrometry*, 23, 1068-1075 (2008)**

**N. Fukuda, A. Hokura, N. Kitajima, Y. Terada, H. Saito, T. Abe and I. Nakai.**

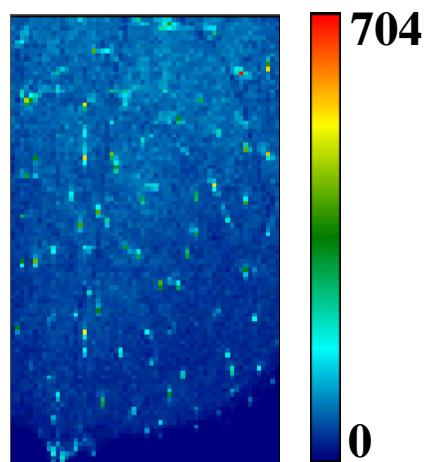


*Arabidopsis halleri* ssp. *Genmifera* (ハクサンハタザオ)

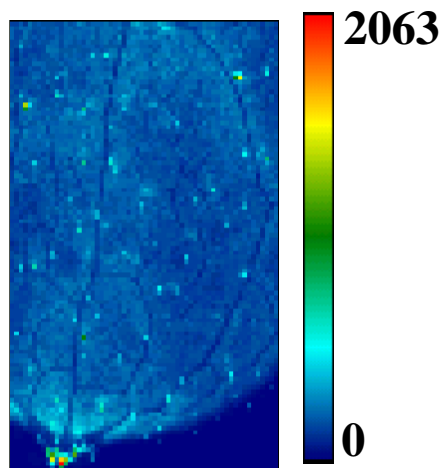


*Arabidopsis halleri* is known as a Cd and Zn hyper-accumulator, which contained more than 9000 mg/ kg Cd and Zn.

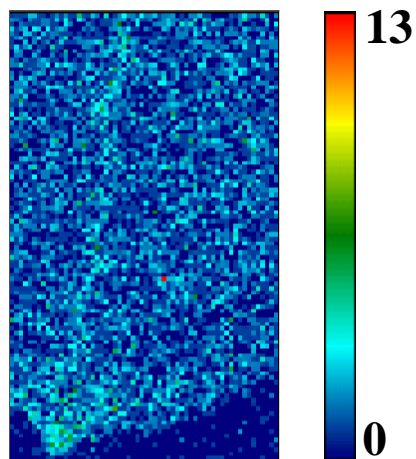
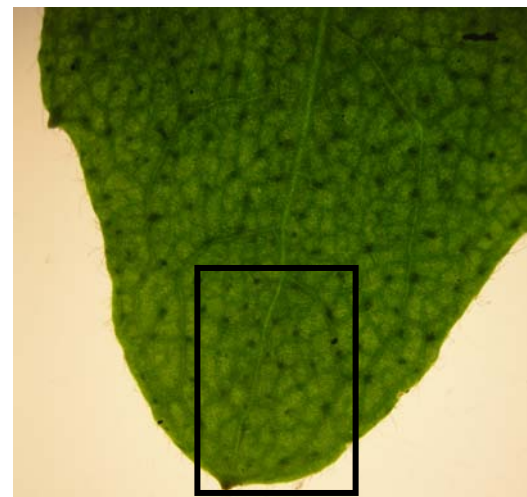
# XRF imaging of a leaf of *A. halleri* ssp. *Gemmifera*.



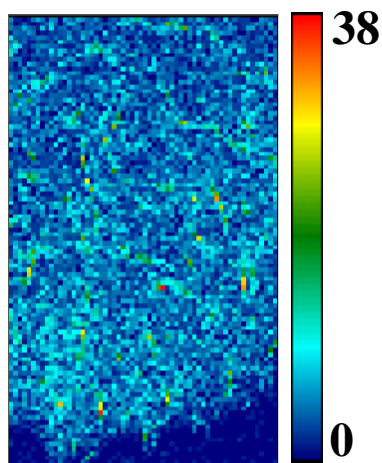
Cd



Zn



Rb



Sr

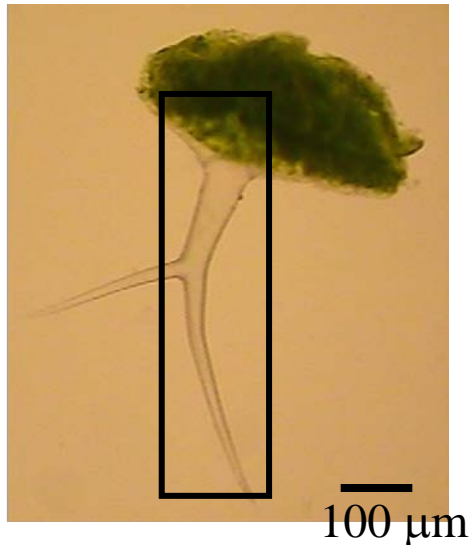
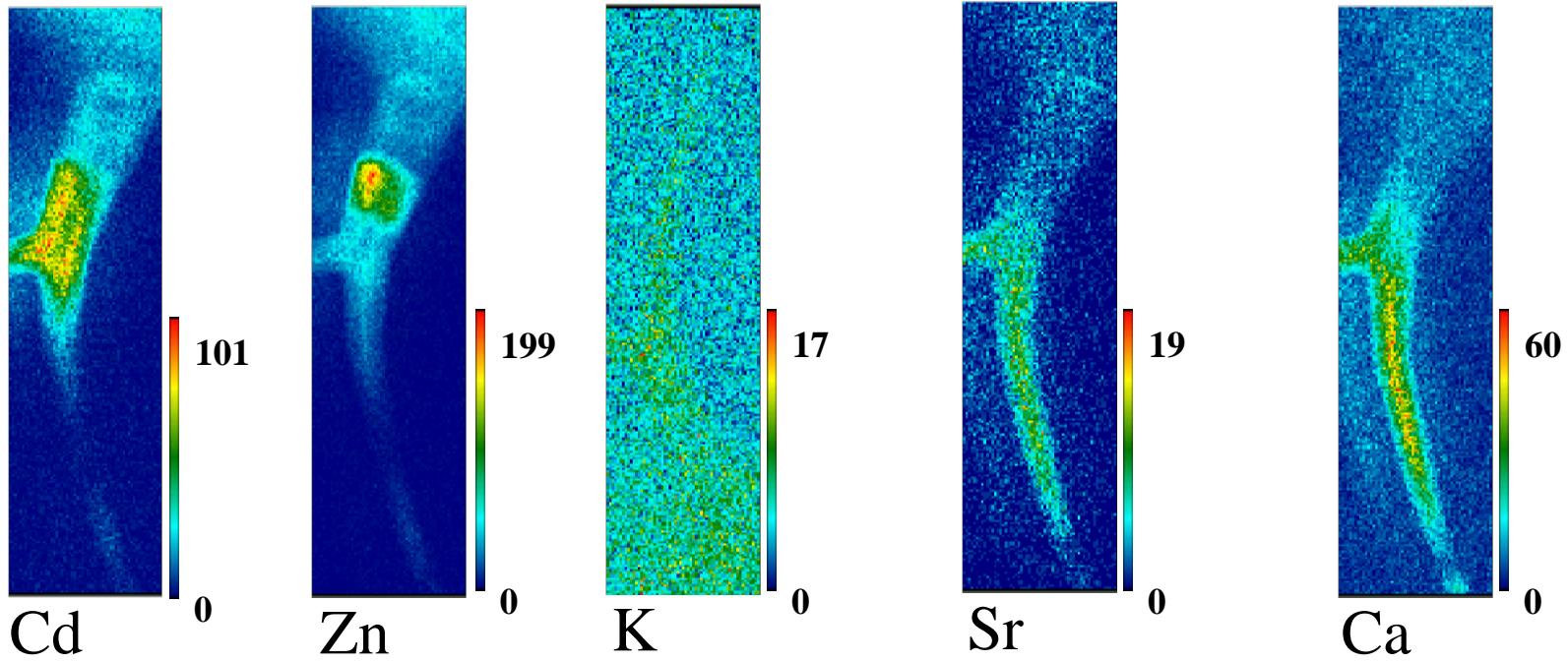
X-ray Energy : **37 keV**

Beam size : **50  $\mu\text{m}$   $\times$  50  $\mu\text{m}$**

Measurement points : **60 point  $\times$  100 point**

measurement time : **1 sec/point**

# $\mu$ -XRF imaging of a trichome taken from a leaf.



X-ray Energy : 37 keV

Beam size : 3  $\mu$ m  $\times$  3  $\mu$ m

Measurement points : 59 point  $\times$  226 point

measurement time : 0.5 s/ point

**Trichomes are epidermal hairs present at the surface of leaves of *A. halleri*, and their functions are thought to be an exudation of various molecules.**

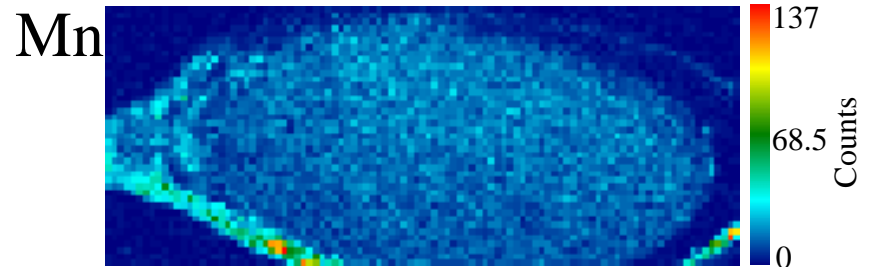
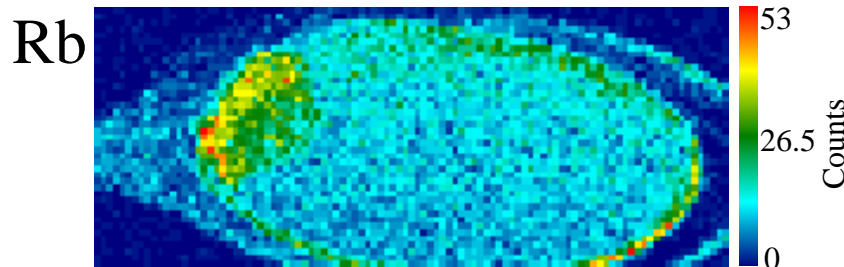
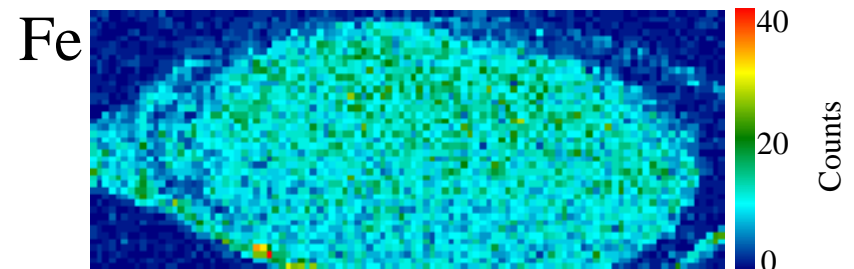
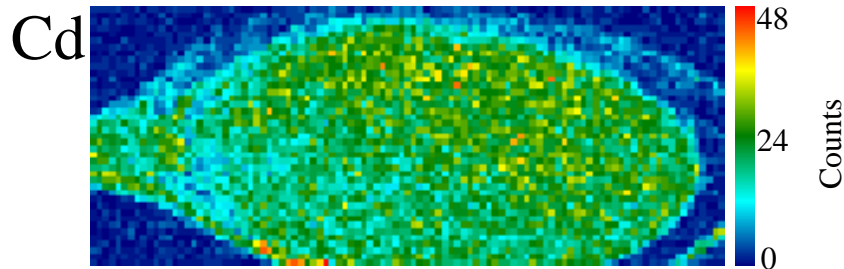
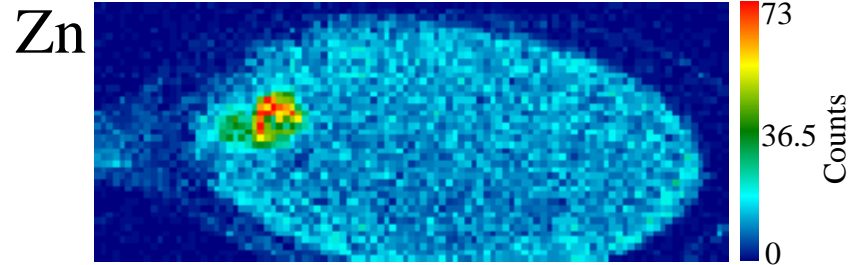
# Brown Rice

Cd 1 ppm solution was added to the soil.

Beam size :  $50 \mu\text{m} \times 50 \mu\text{m}$

Measurement points :  $101 \times 41$  points

Exposure time : 2 s/point



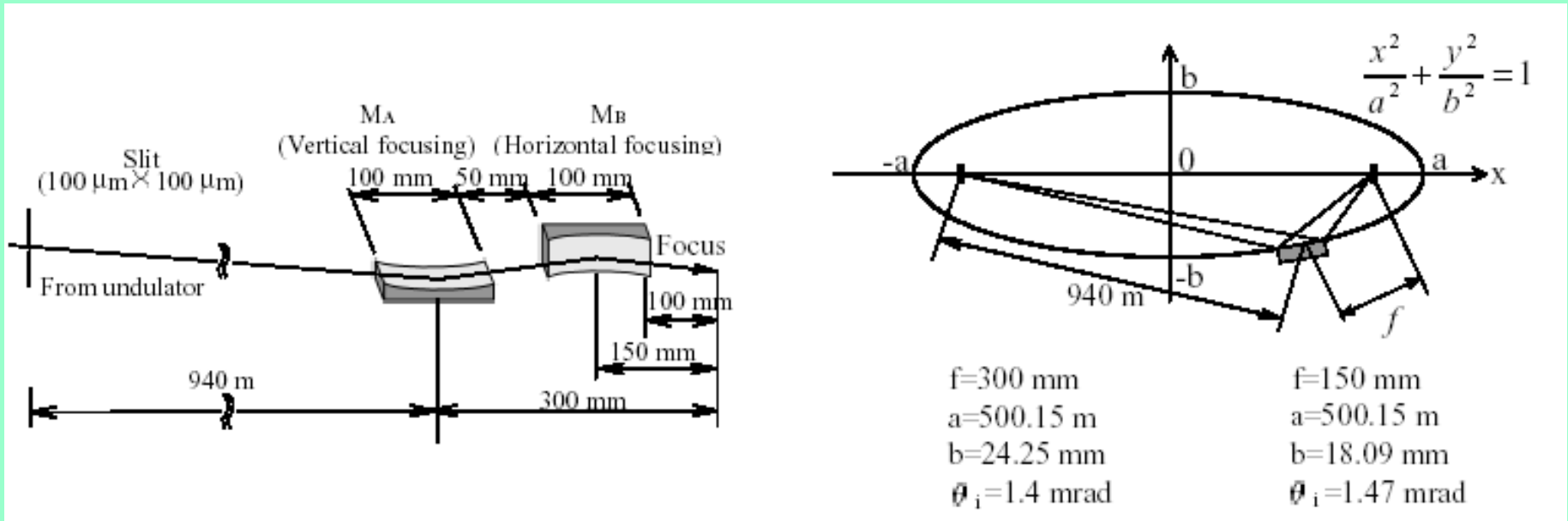
Cd was in the whole tissue, but Zn was localized in the embryo.

## Summary

- $\mu$ -XRF imaging technique utilizing SR can monitor time dependent process of arsenic transfer in a leaf tissue of hyperaccumulator fern.
- It is possible to visualize arsenic transfer from root to marginal part of leaf within 30min after feeding.
- Cell level element analysis and chemical state analysis of Cd in the plant is possible

# Prospect of microbeam analysis

## Microbeam $\rightarrow$ Nanobeam

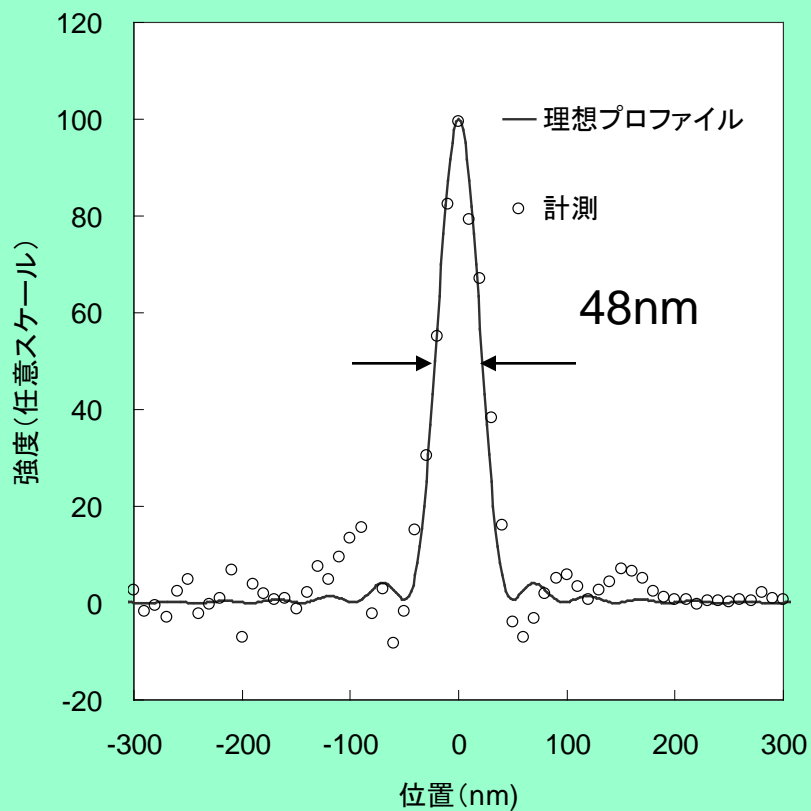


## Nano-beam focusing system at SPring-8

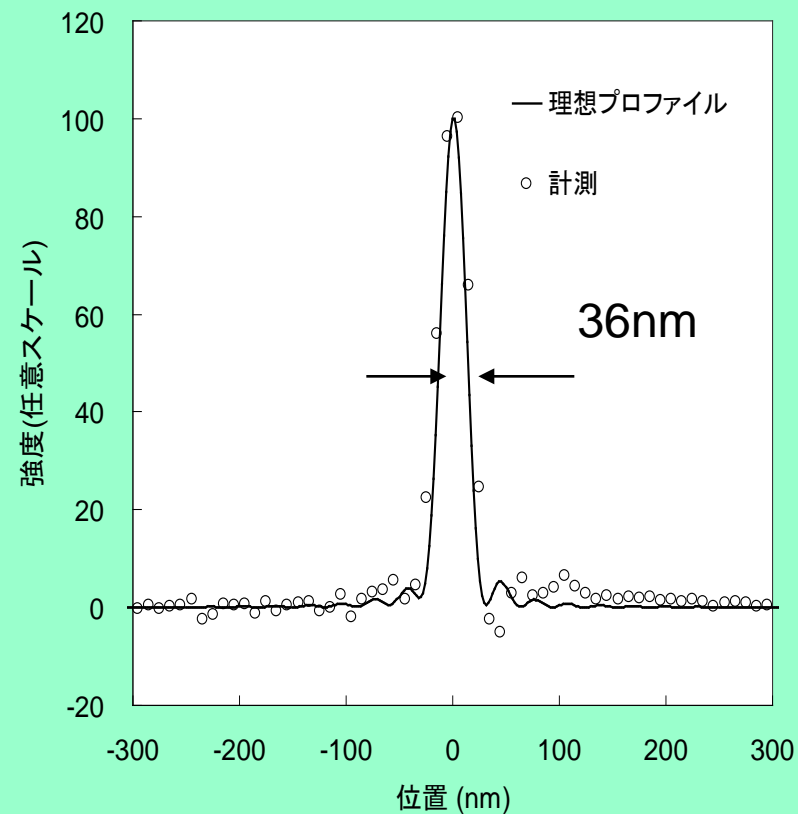
(left) High precision K-B mirror

(right) Optical parameters of elliptical mirror

Yamauchi et al. (Osaka Univ.)

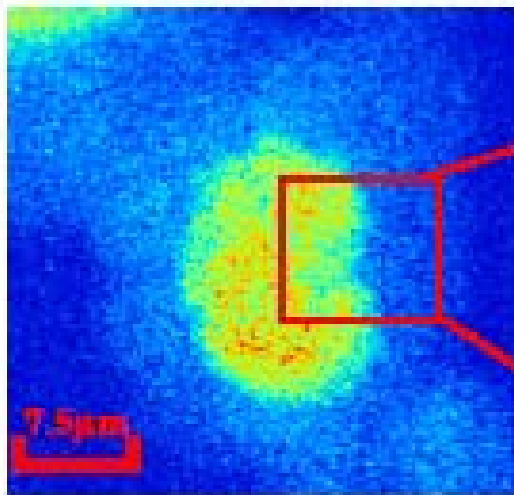


(a)vertical

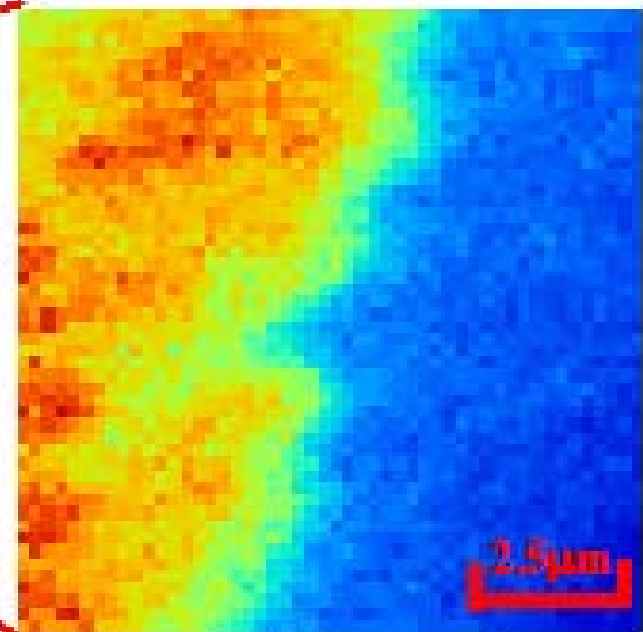


(b)horizontal

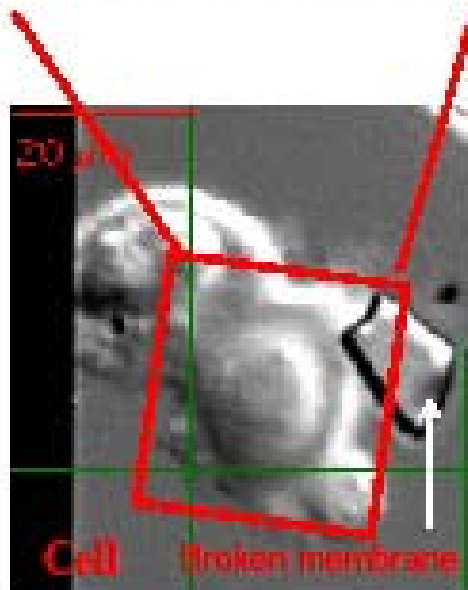
Beam profile



*Full image of cell as iron mapping*



*Iron mapping in a part of a nucleus*



**Opt. microscope**

*Experimental condition of the iron mapping*

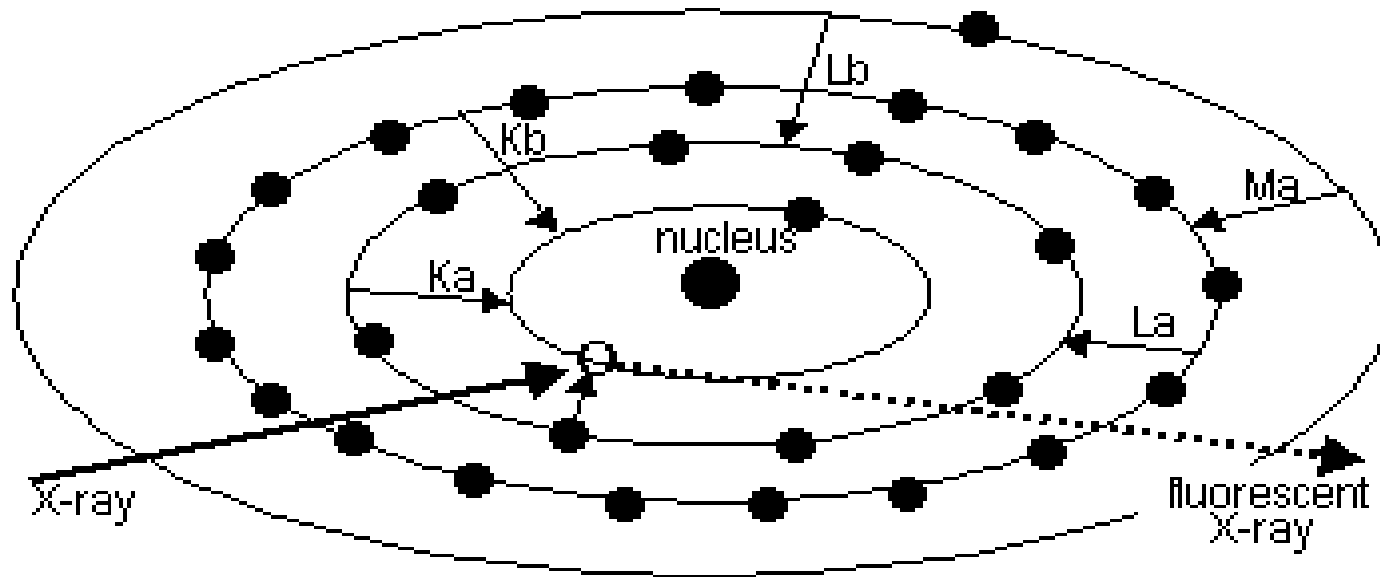
<b>Sample</b>	<b>Human cell</b>
<b>X-ray Energy</b>	<b>15keV</b>
<b>Beam size</b>	<b>200nm x 200nm</b>
<b>Scanning pitch</b>	<b>200nm/pixel</b>
<b>Scan area</b>	<b>10μm x 10μm</b>

**Organelle level analysis**



(4)High energy X-ray

# High energy SR-XRF



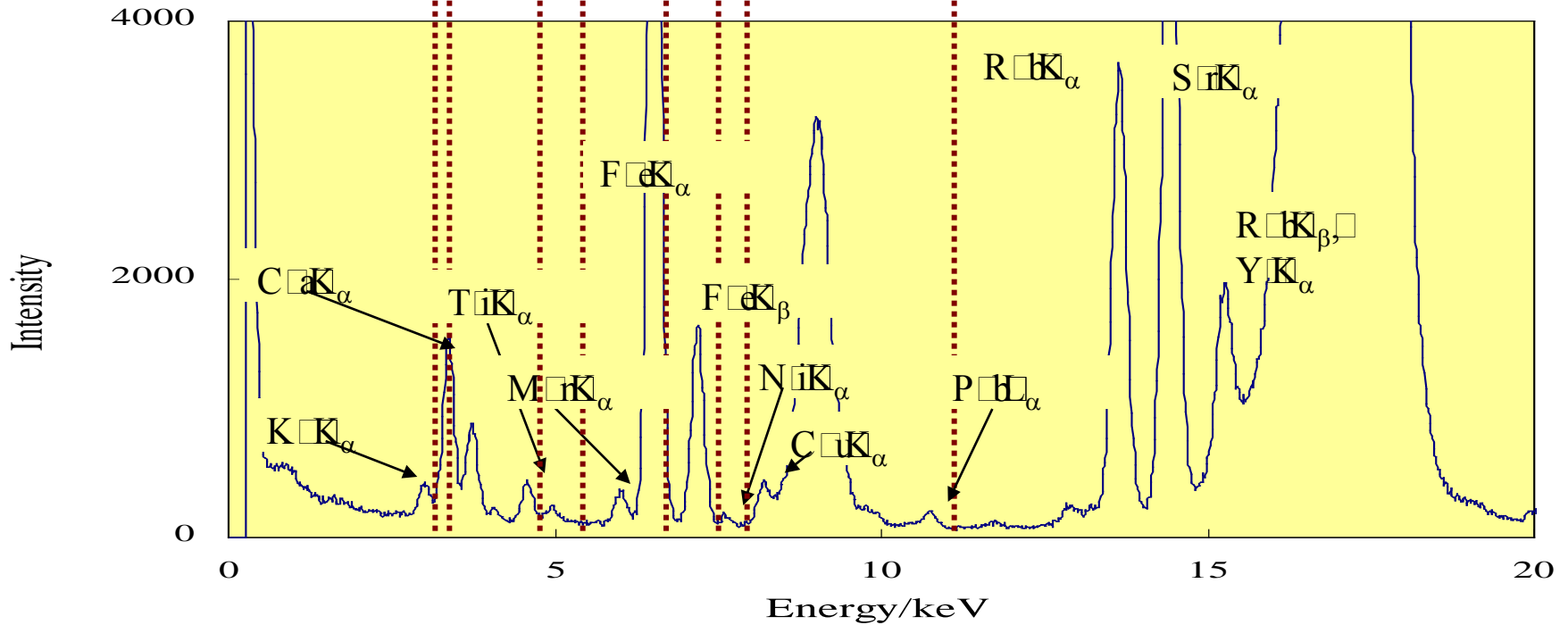
Highest energy

Bi K $\alpha$  76.35  $E_b=90.57$

U K $\alpha$  97.17  $E_b=115.66\text{keV}$

Positions of the L lines in

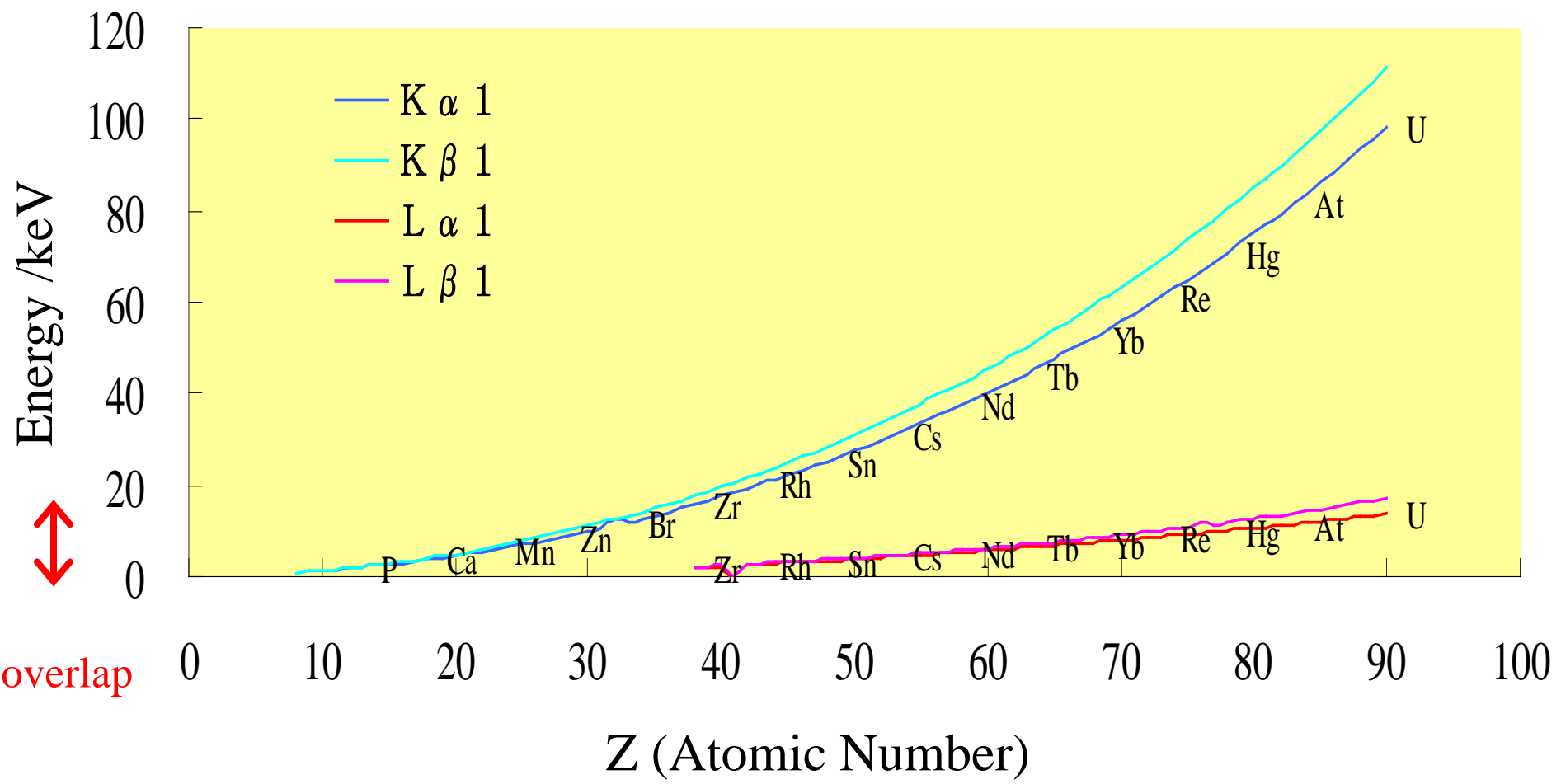
Sn Sb La Nd Dy Lu Bi



Problem of conversion ( $E < 20$ )

Overlap of heavy elements L

Sample:  $Md K_{\alpha}$  X-ray, 40 mA, t



## X-ray fluorescence energies of K & L lines v.s. atomic number

L line for all elements    20 keV >

Above 20 keV → K line only

→ suitable for analysis of elements heavier than Rh K $\alpha$  (= 20.17 keV)

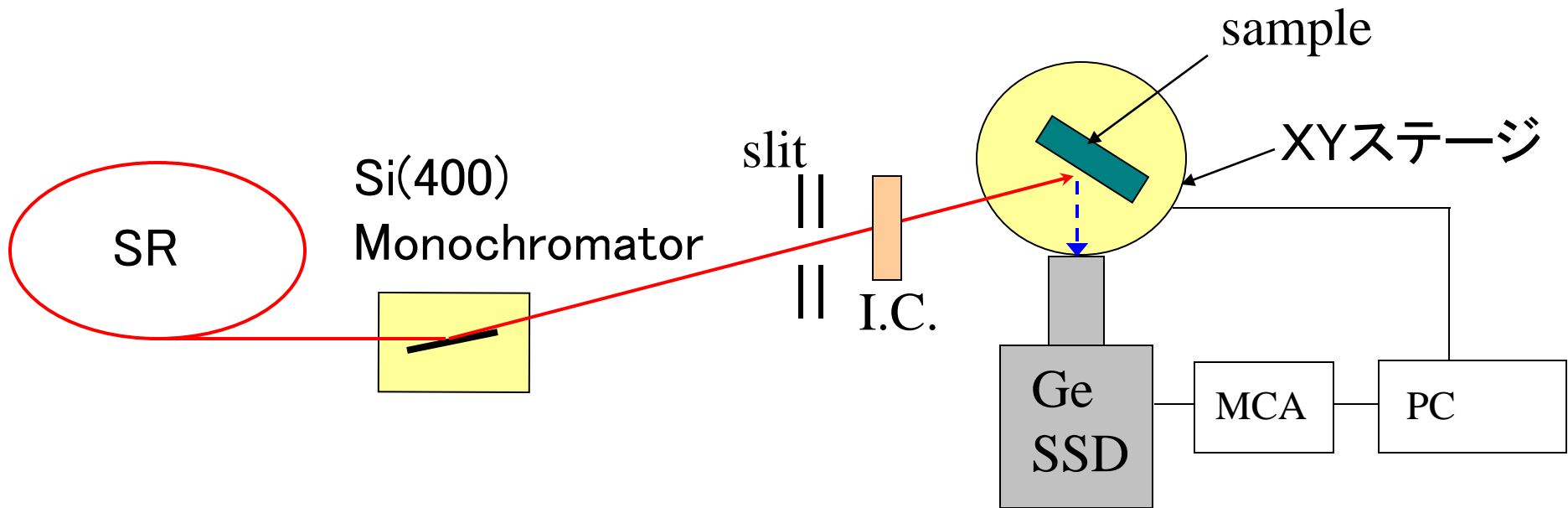
## ◆ Advantage of high energy XRF

- High sensitive analysis of trace heavy elements by excitation of K-shell electrons of heavy elements
- Low absorption effect and high penetration depth

## ◆ Application field of high energy XRF

Heavy elements ( Lanthanoid elements, U, Nb, Zr, Hf, W, Cd, Hg etc. ) are important in industry ( high-Tech materials) , environmental science, geochemistry, archaeology, forensic science for provenance analyses.

# BL08W (for High-energy inelastic scattering experiments)

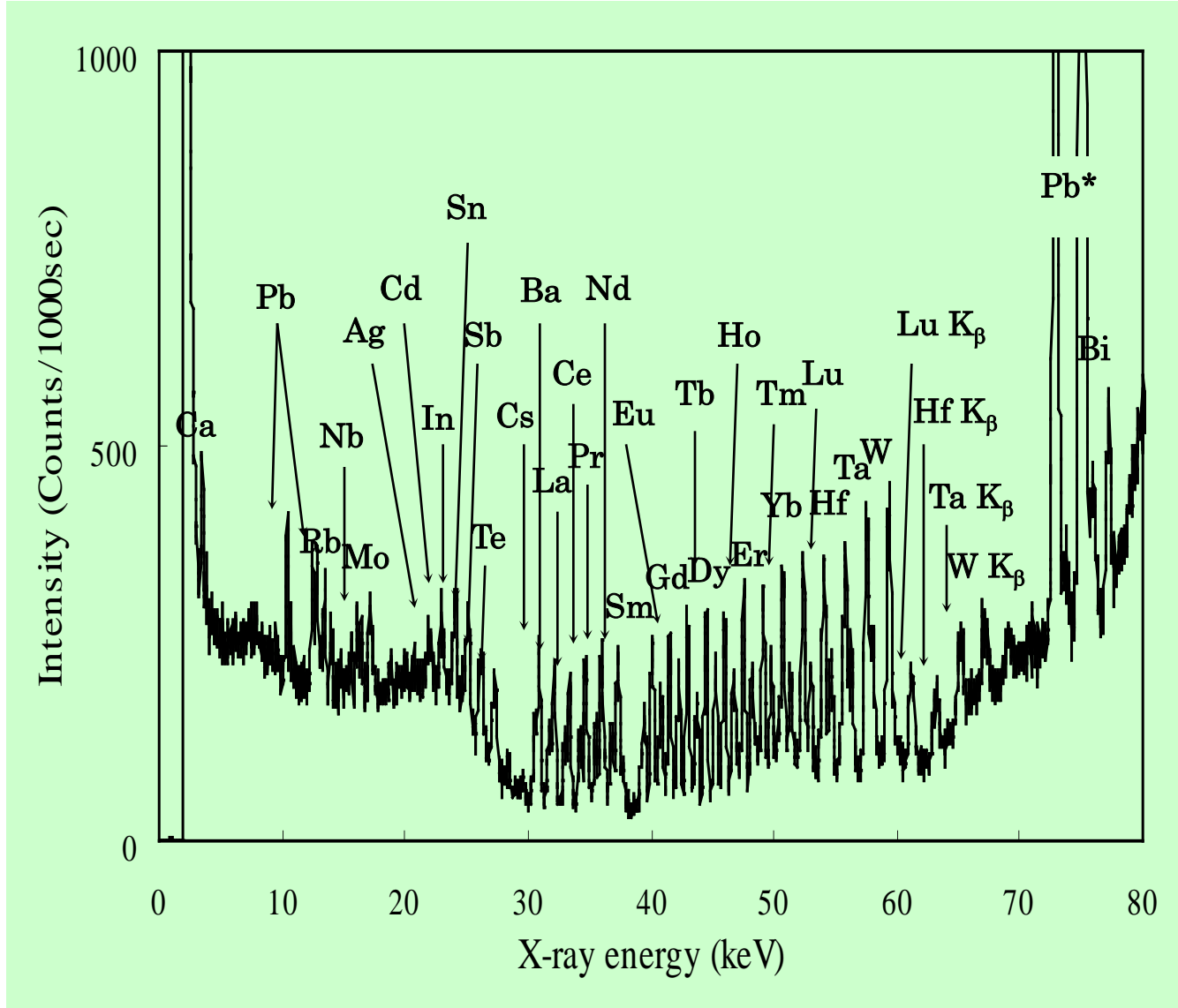


Elliptical multipole wiggler (Gap:160~25.5 mm)

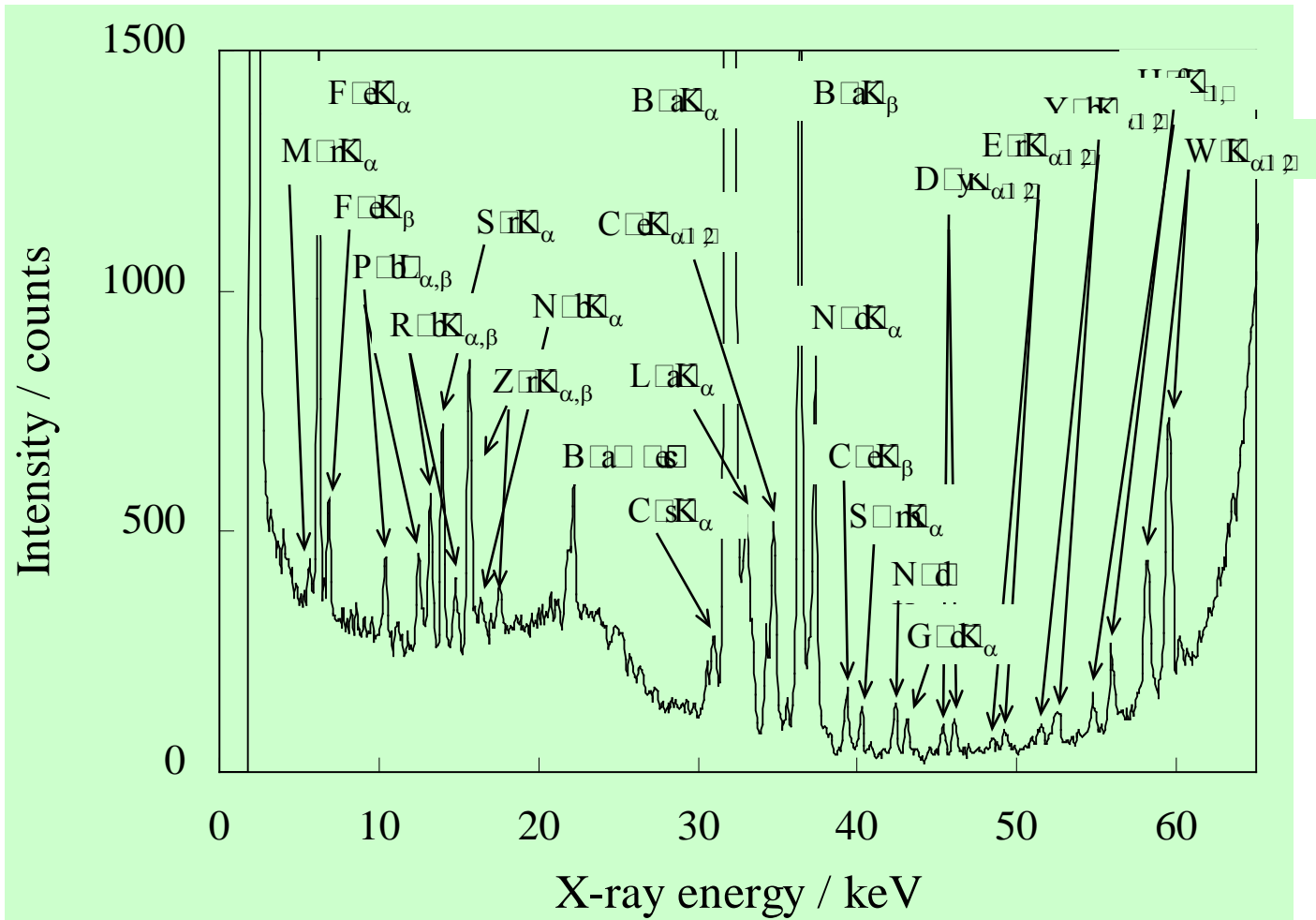
Excitation energy:116 keV (100–150 keV)

Beam size:1~0.1 mm<sup>2</sup>

Experimental setup for high energy XRF



**XRF spectrum of NIST SRM612 glass:  
61 trace elements in 50ppm level(\*scattering)**



XRF spectrum of an excited standard at 116 kV

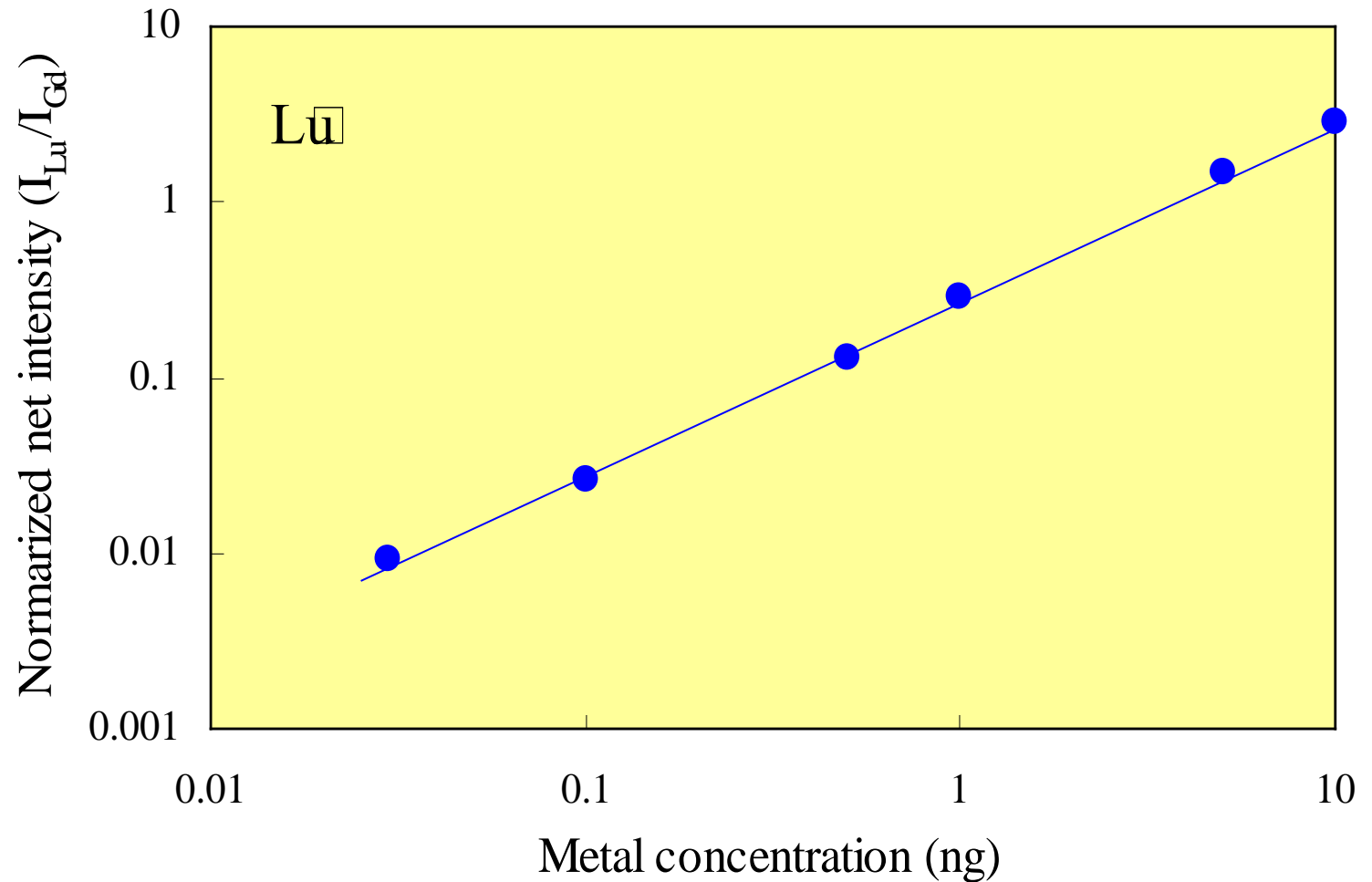


## MDL for JG1 sample

---

Contents/ ppm	I <sub>peak</sub>	I <sub>back</sub>	MDL/ppm	
Fe	2.02 <sup>a)</sup>	1557	366	0.097 <sup>a)</sup>
Rb	181	577	281	30.8
Sr	184	719	258	19.2
Zr <sup>b)</sup>	108	395	293.5	54.7
Cs	10.2	280	181	4.2
Ba	462	7205	354.5	3.8
La	23	535	355.5	7.2
Ce	46.6	520	86	3.0
Nd	20	862	154.5	1.1
Sm	5.1	136	45	1.1
Gd	3.7	108	42.5	1.1
Dy	4.6	110	41	1.3
Er	1.7	86	51.5	1.1
Yb	2.7	125	61	1.0
Hf	3.5	268	98.5	0.6
W	1.7	737	199.5	0.1

---



**Calibration curves for Lu  
using K-lines XRF spectra**

## . Application field of high energy XRF

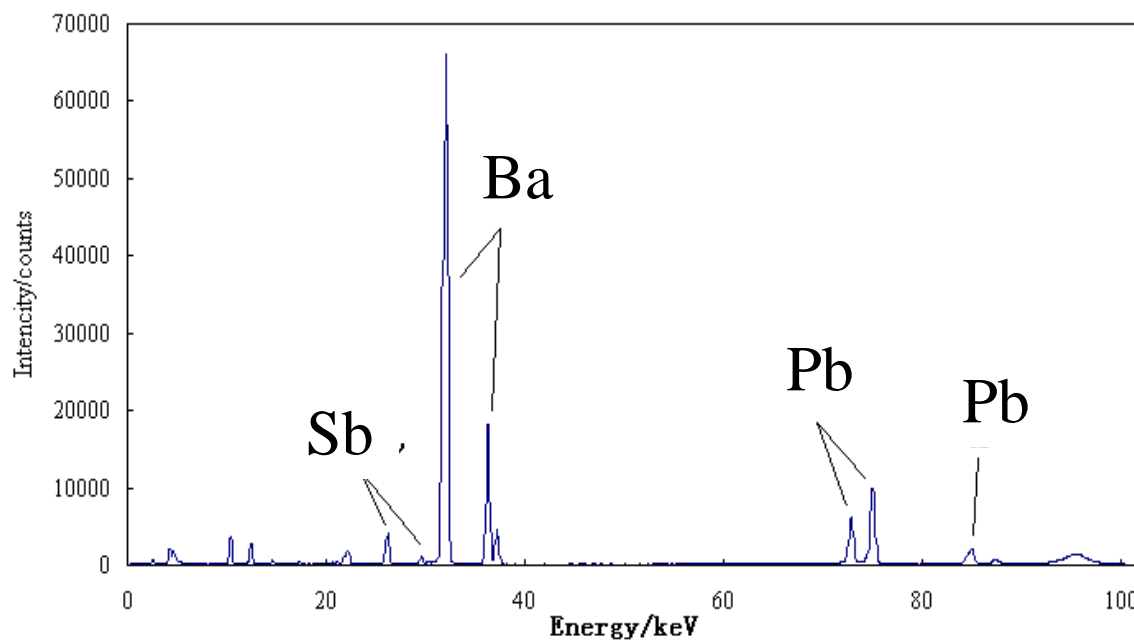
- Archaeology : nondestructive provenance analysis
- Forensic analysis
- Industrial chemical analysis of high-Tech materials
- Geochemistry

# Forensic application

## S & W Gunshot Residue



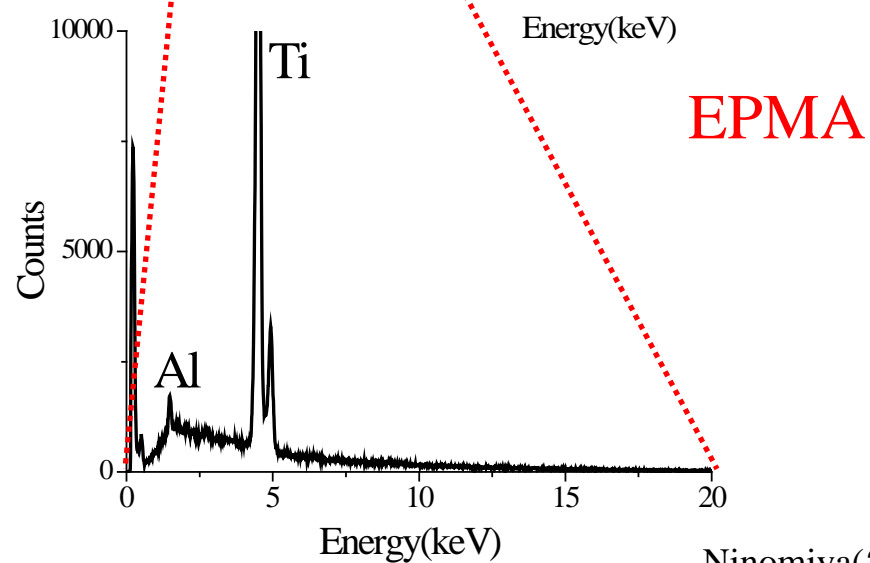
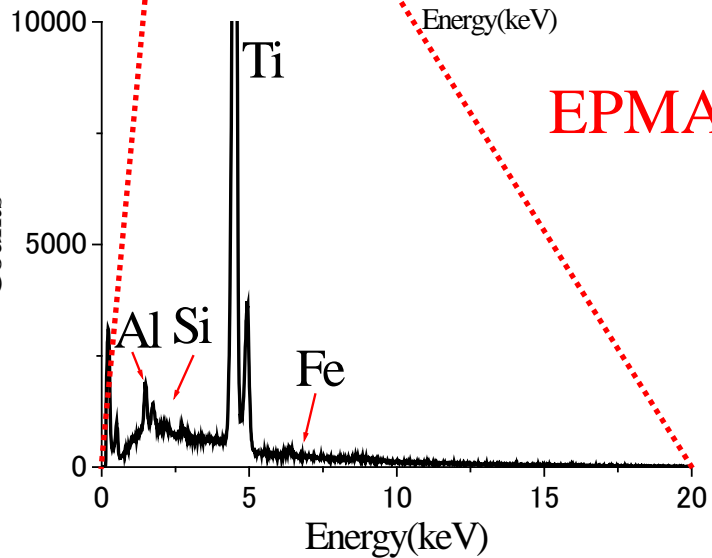
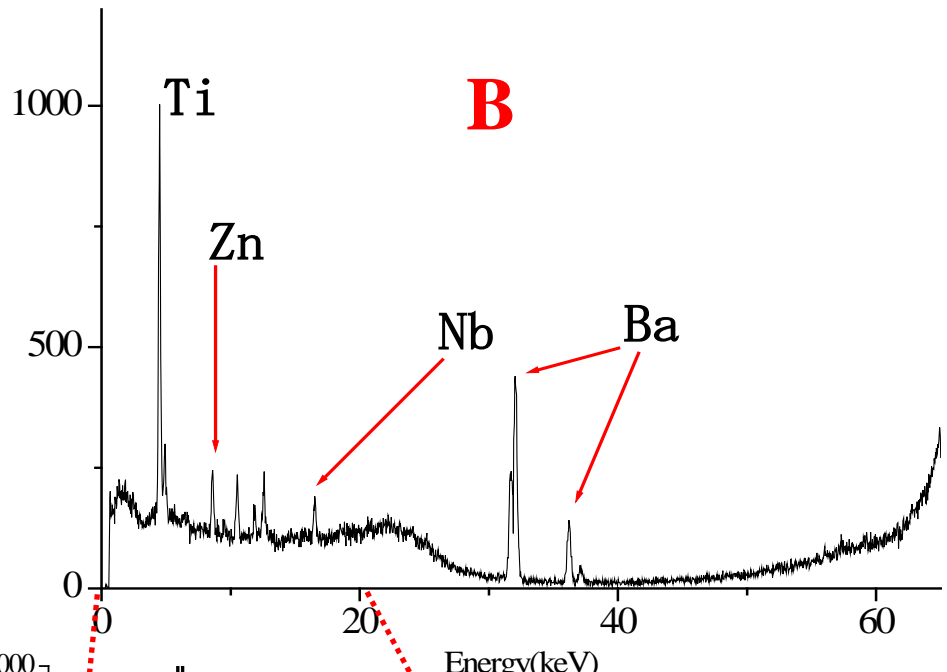
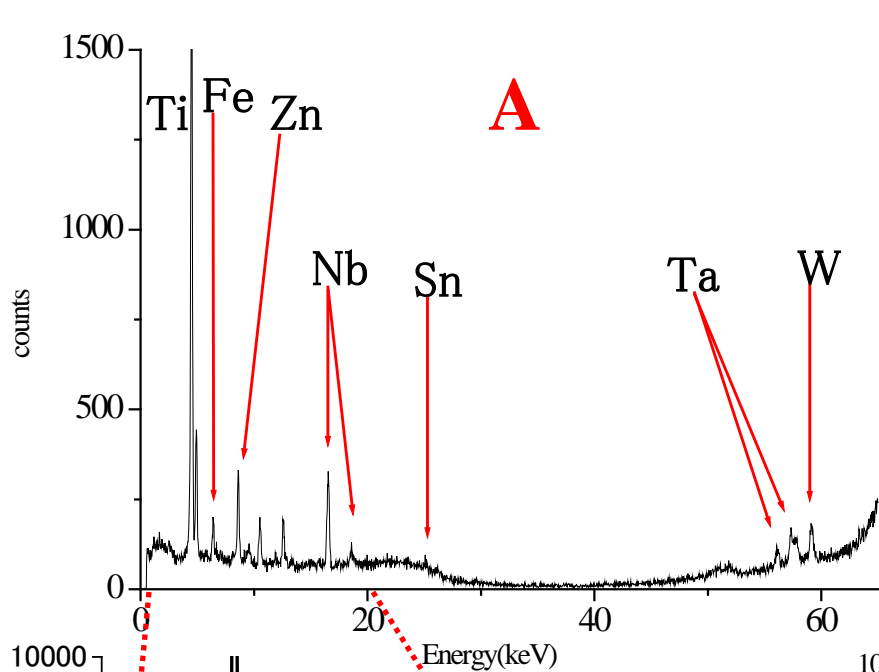
**Characteristic element: Ba, Sb, Pb**



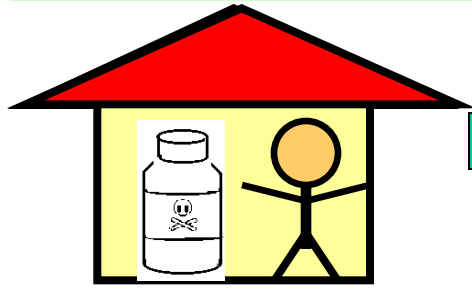
**SPring-8 BL08W**

**High energy SR-XRF characterization of trace gunshot residue**

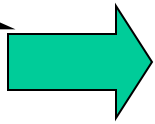
# High energy XRF characterization of trace heavy elements in white car paints (paints A & B) compared with X-ray microprobe (bottom)



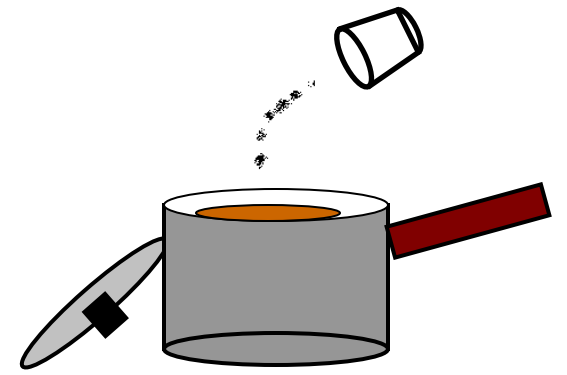
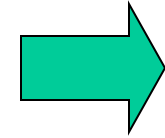
Forensic analysis



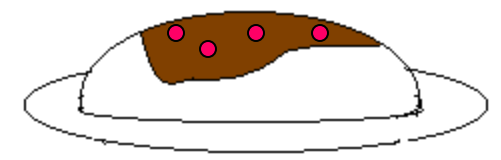
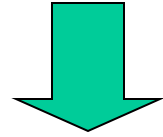
As<sub>2</sub>O<sub>3</sub>



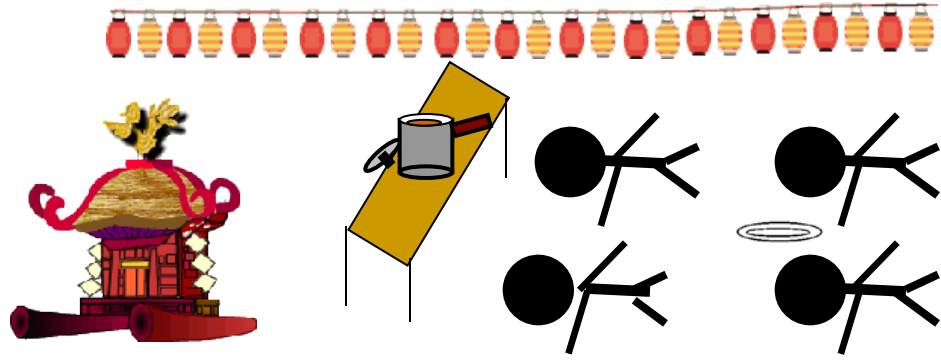
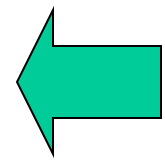
Paper Cup



Cooking



Curry Rice



Forensic application: Arsenic Murder case

Date: July 25 , 1998

Place: Festival Site at Sonobe , Wakayama Pref. JAPAN

Acute Arsenic intoxication : Death 4

Injured 63

# Material evidence around the crime

## Arsenic oxides:

- in the curry
- adhered to a paper cup found at the festival site, dumping ground
- on a plastic container found in the kitchen of a woman whose husband used arsenic oxide in his job as a professional exterminator of white ants
- five samples of arsenic sized from around their house

# Requests and Solution

- Analysis of **Bi,Sb,Sn in ppm** level in the sample of **0.01mg** in less than three weeks

X-ray fluorescence analysis utilizing **116keV**

X-rays from SR ( New approach ) →

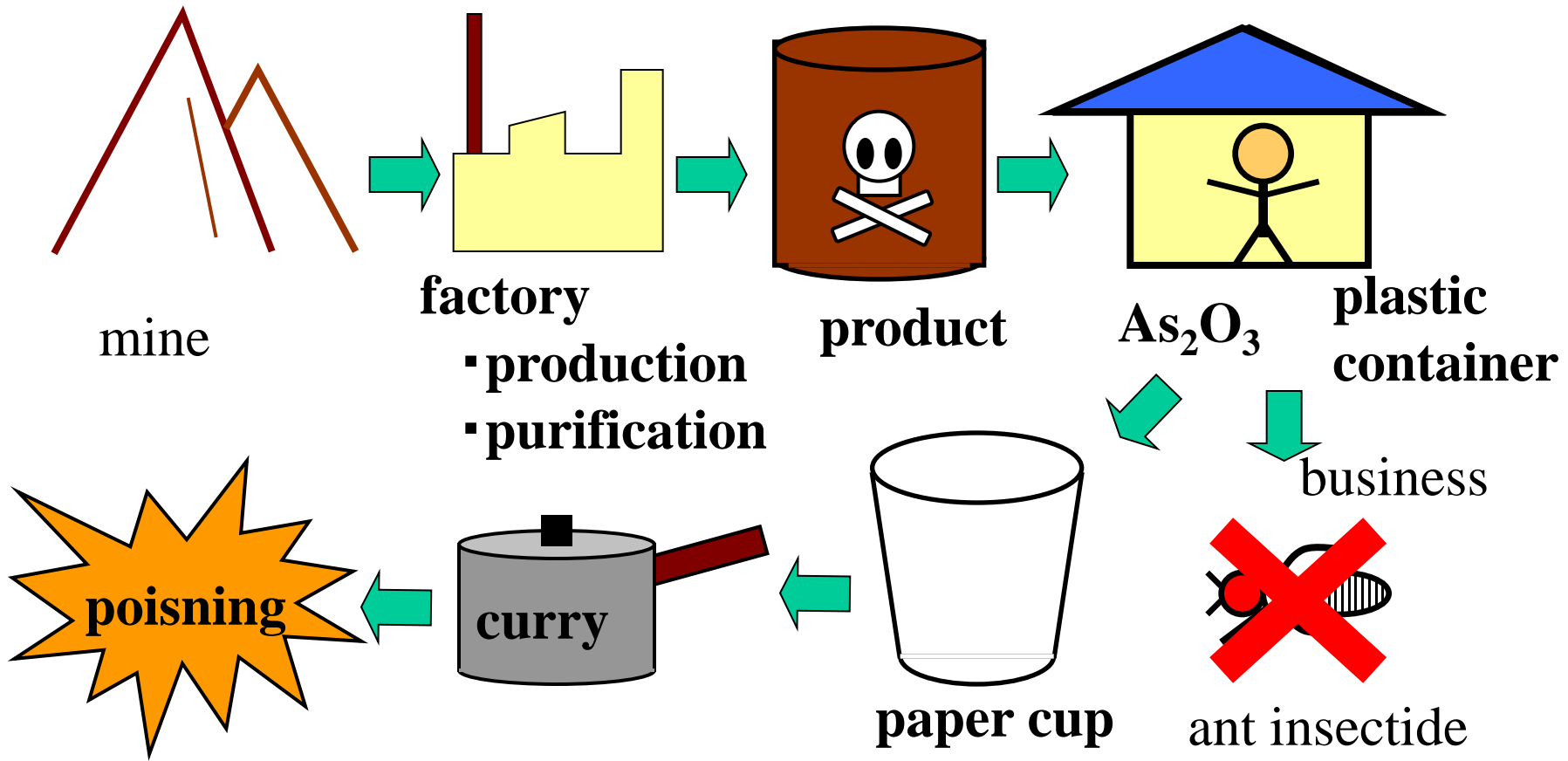
Heavy element analysis by **K-line X-rays** allow good separation of the peaks of the elements in the XRF spectrum without any interference of light elements.



## Problems

- In total, police seized eight kinds of arsenic oxide samples as evidence but there was no proof connecting them. Especially the amount of the sample (ca.0.01mg) adhered to the plastic container was too small to be analyzed by any conventional analytical techniques at the National Scientific Criminal Investigation.

Principle of identification :material history of arsenic trioxide →heavy elements impurity:  
Sb,Bi Sn,Mo



# Experimental Results and Interpretation

- Characteristic features of being common in the appraisal samples
  - ◆ Existence of Mo only in the appraisal samples
  - ◆ Sn and Sb exist in nearly equal amount level while the Bi level is 2 or 3 times higher than the Sn and Sb levels
- The probability of the coincidence  
 $= Mo \times Sn \times Sb \times Bi$
- Conclusion
  - The eight samples all arsenic trioxide from the same source
    - Public Prosecutor's Office.
    - This crime is now under justice.

## **(5) Multiple X-ray analytical technique**

**A combination of  $\mu$ -XRF imaging, m-XRD, XAFS and SEM**

**Chemical speciation of arsenic-accumulating mineral in a sedimentary iron deposit by synchrotron radiation multiple X-ray analytical techniques**

S.ENDO, Y.TERADA, Y.KATO, I.NAKAI  
Environ.Sci.Technol.2008,42,7152

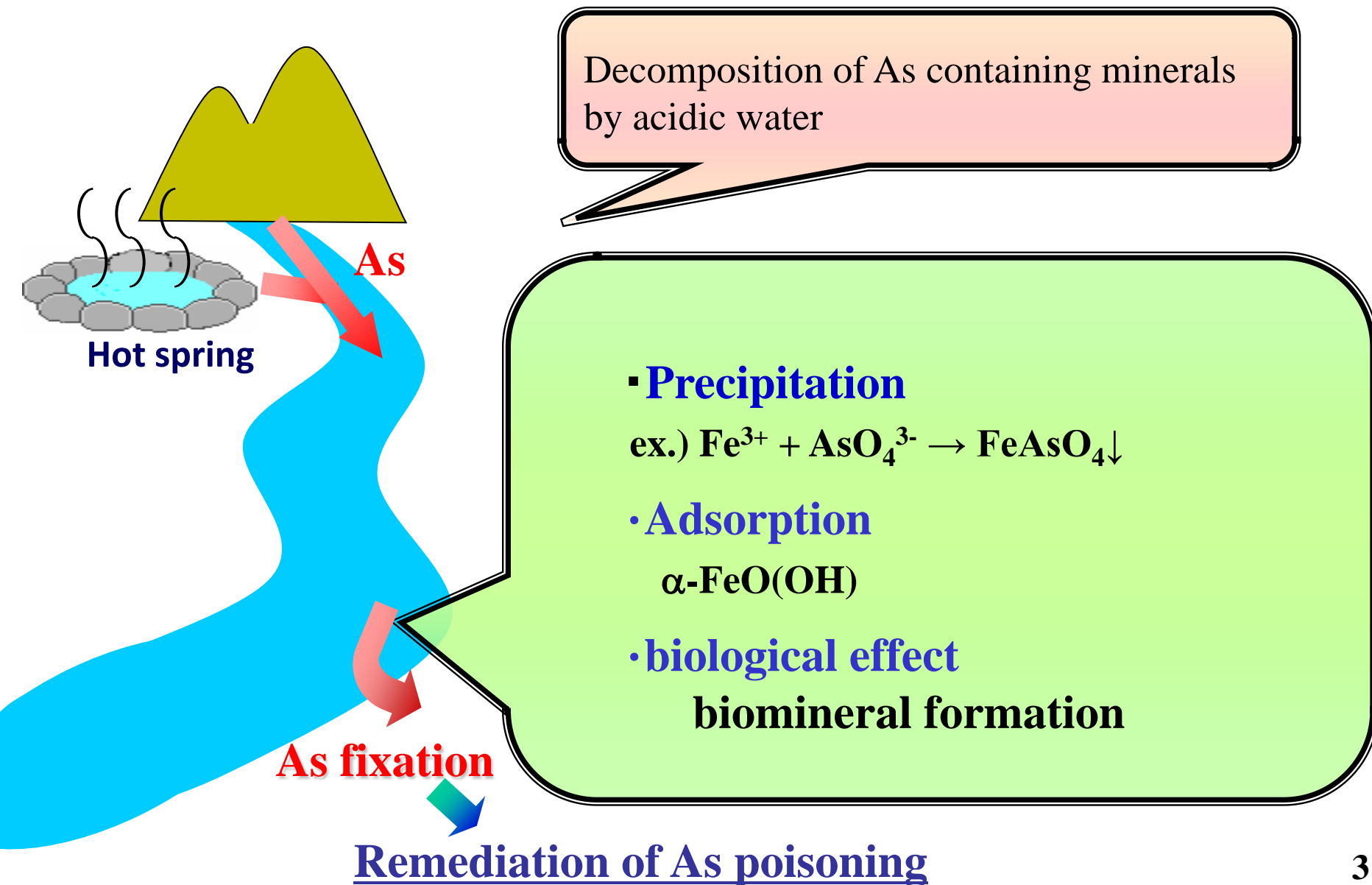
Comprehensive characterization of As(V)-bearing iron minerals from the Gunma iron deposit by



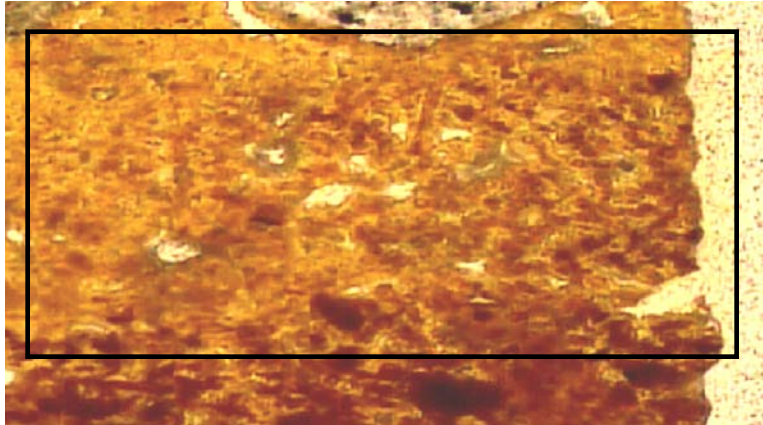
Sample the Gunma iron deposit of quaternary age

# Background

Natural behavior of arsenic at volcanic region



# SR- $\mu$ -XRF XRF imaging



200  $\mu$ m

SPring-8 BL37XU

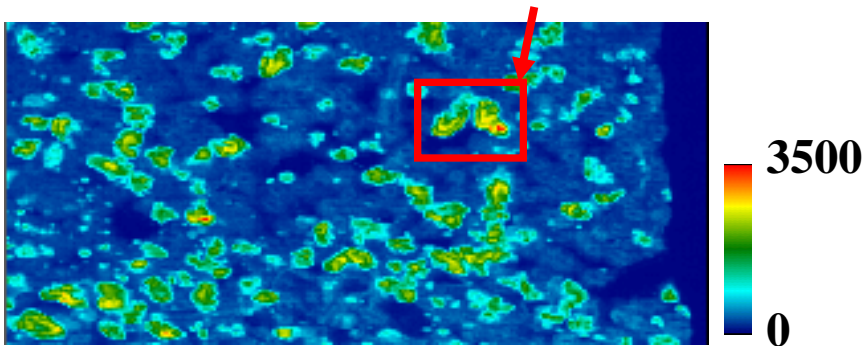
X-ray: 12.8 keV

Beam size : 1.8  $\mu$ m  $\times$  2.8  $\mu$ m

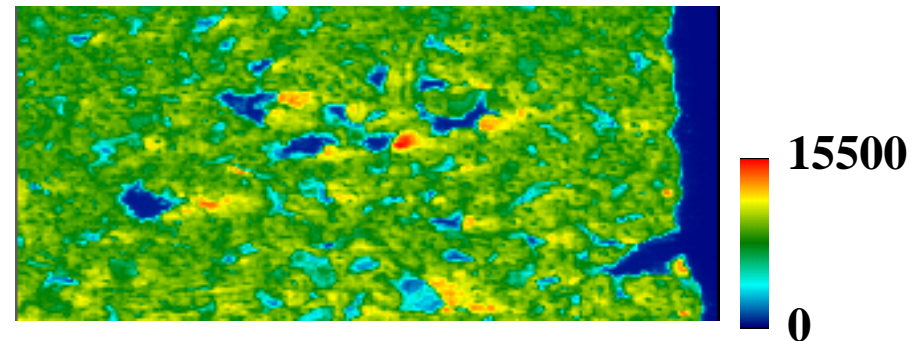
Step size : 2.0  $\mu$ m  $\times$  3.0  $\mu$ m

Meas. time : 0.1 s/point

Detector : SDD



As



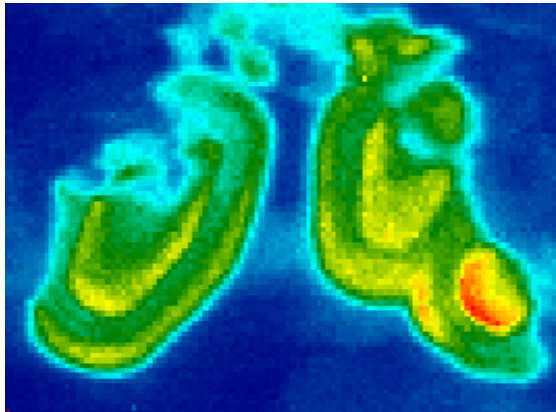
Fe

Purpose: which mineral accumulate arsenic?

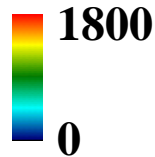
strengite  $\text{FePO}_4 \cdot 7\text{H}_2\text{O}$  ?  
jarosite  $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$  ?  
goethite  $\text{FeOOH}$  ?

# SR- $\mu$ -XRF & SEM-EDS

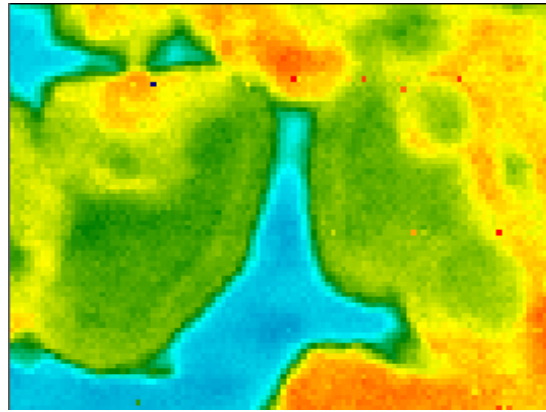
strengite  $\text{FePO}_4 \cdot 7\text{H}_2\text{O}$   
jarosite  $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$



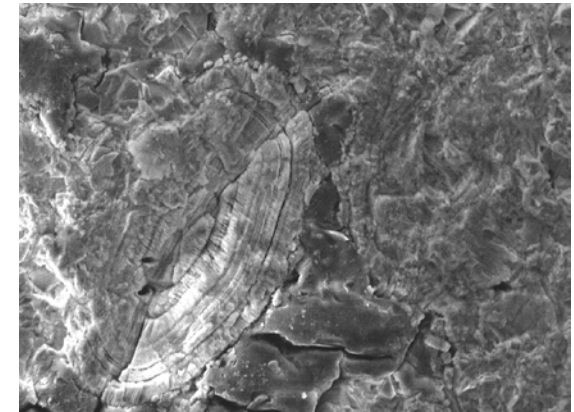
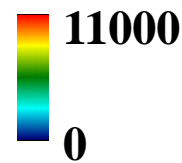
As



Beam size:  $1.8 \mu\text{m} \times 2.8 \mu\text{m}$   
Step size :  $1.0 \mu\text{m} \times 1.0 \mu\text{m}$



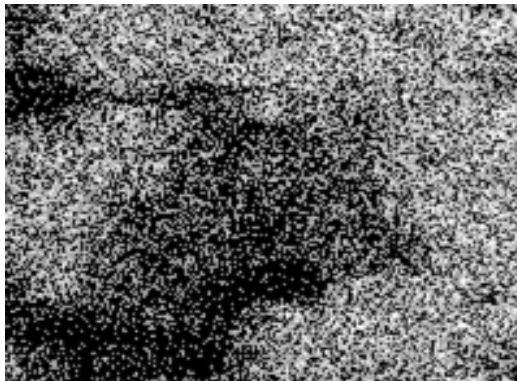
Fe



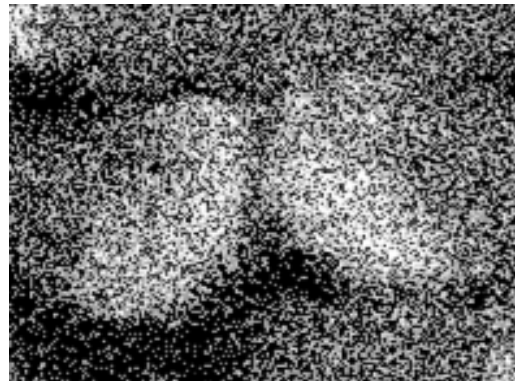
SEM image

20  $\mu\text{m}$

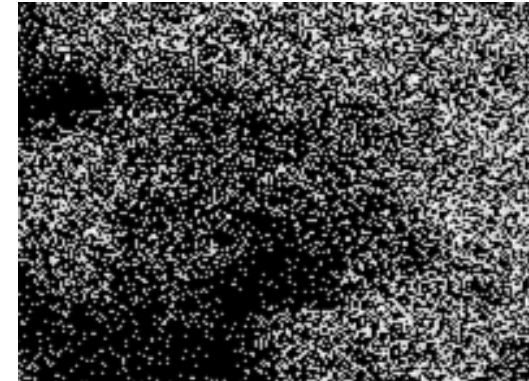
As at the region with peculiar concentric morphology



S (SEM-EDS)



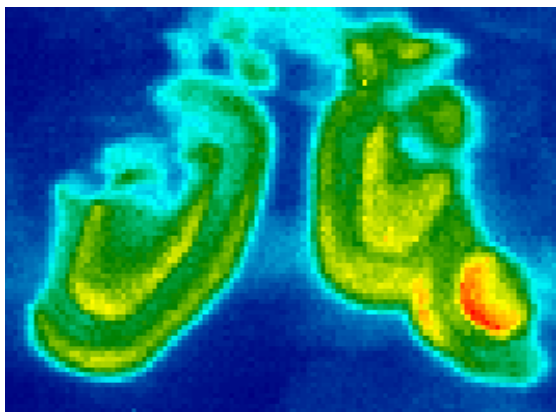
P (SEM-EDS)



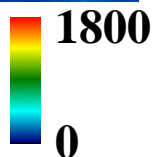
K (SEM-EDS)

Positive correlation between As and P, negative for S and K

# SR- $\mu$ -XRF & SEM-EDS



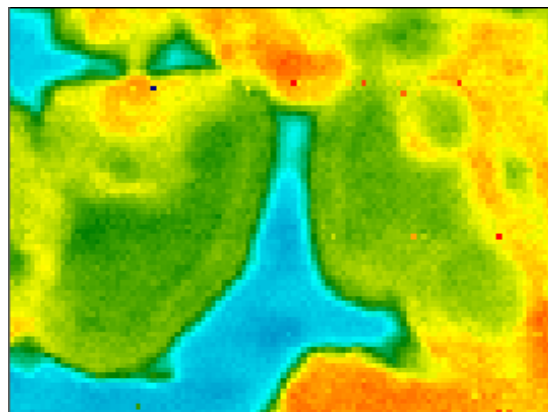
As



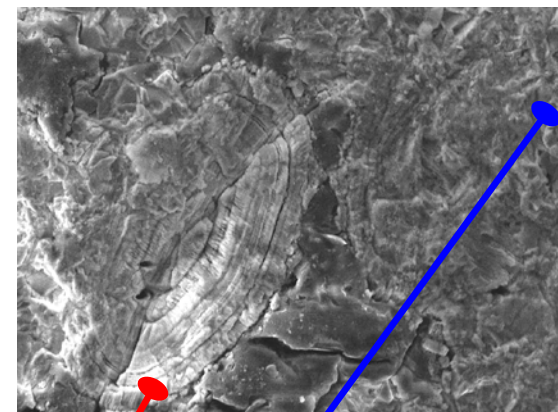
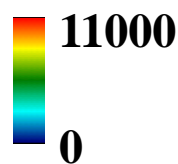
Beam size:  $1.8 \mu\text{m} \times 2.8 \mu\text{m}$   
Step size :  $1.0 \mu\text{m} \times 1.0 \mu\text{m}$

Localization of As.

strengite  $\text{FePO}_4 \cdot 7\text{H}_2\text{O}$   
jarosite  $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$

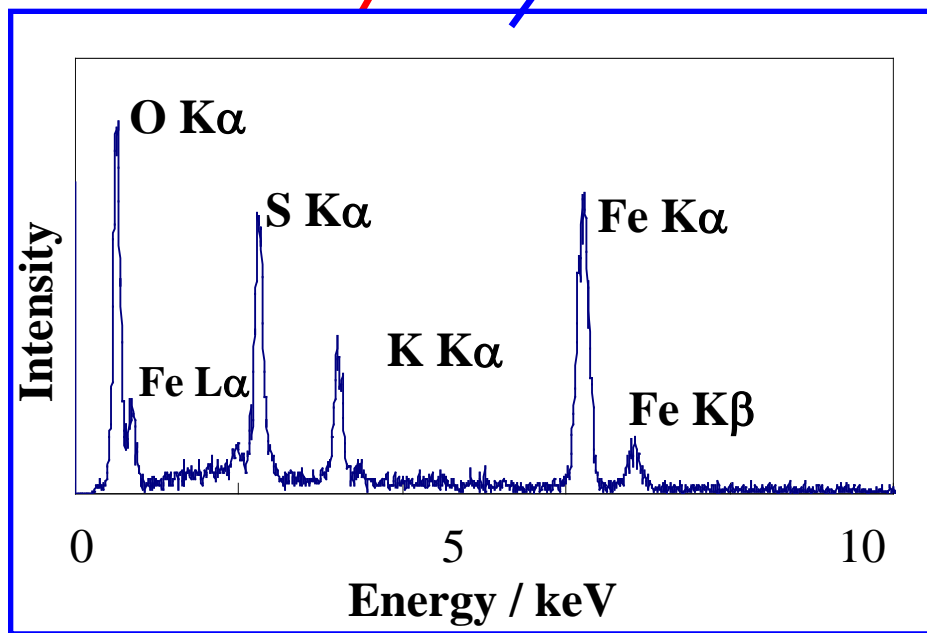


Fe



SEM

20  $\mu\text{m}$



SEM-EDS spectrum



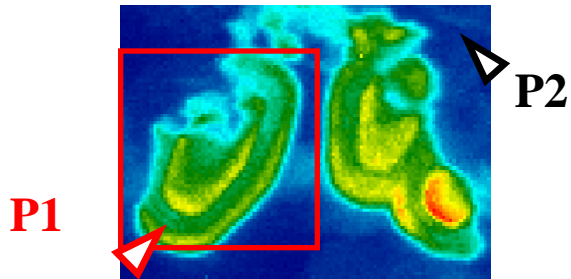
# XRD

X-ray : 12.8 keV

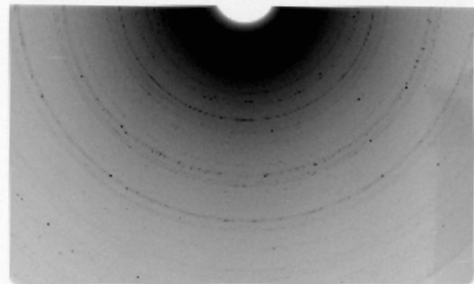
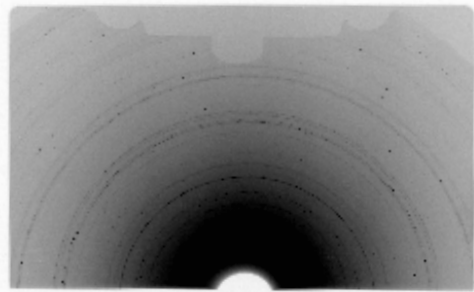
Beam size : 50  $\mu\text{m}$   $\times$  50  $\mu\text{m}$

Meas.time : 12 min. / sample

IP (Imaging Plate)



XRD point



XRD pattern (P1)

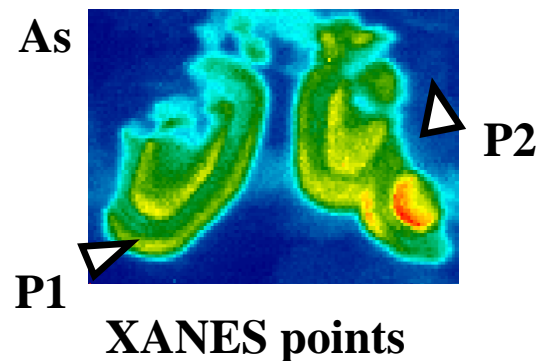
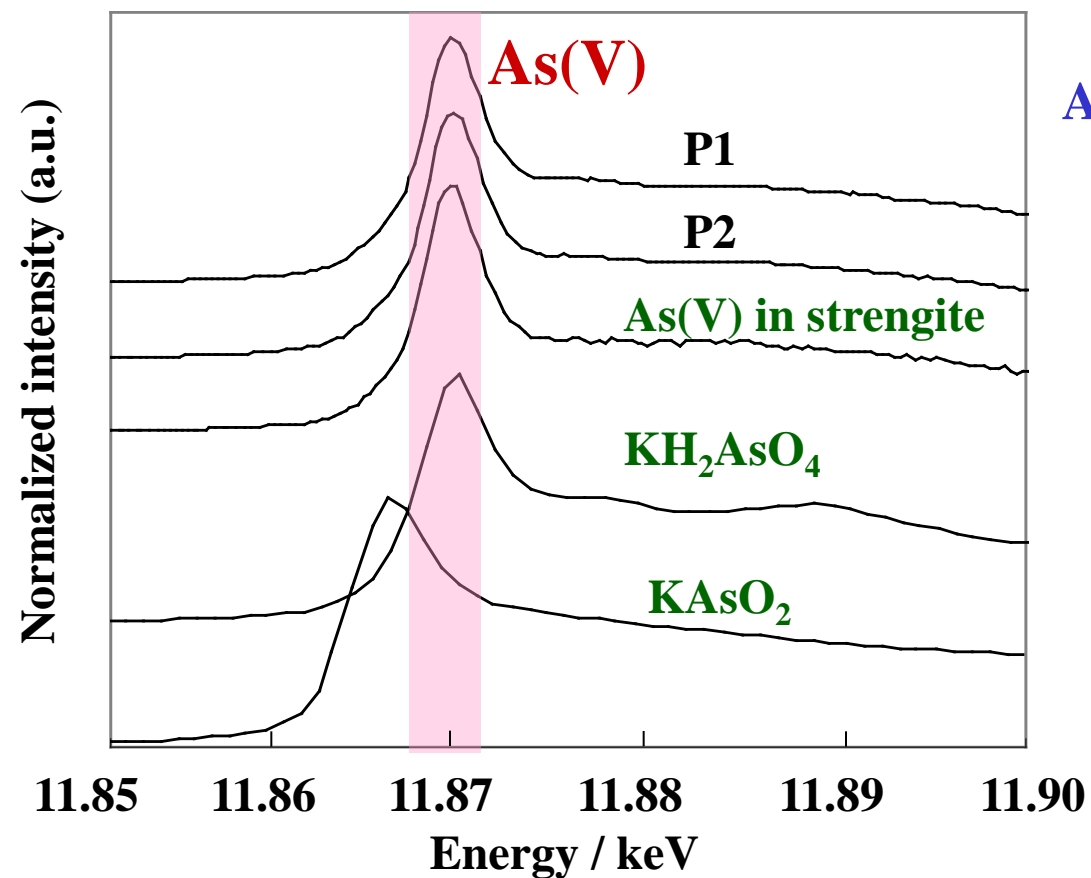
P1		P2		strengite			jarosite		
$d/\text{\AA}$	$I/I_0$	$d/\text{\AA}$	$I/I_0$	$hkl$	$d/\text{\AA}$	$I/I_0$	$hkl$	$d/\text{\AA}$	$I/I_0$
		5.93	32				101	5.93	45
		5.75	14				003	5.72	25
5.49	55			111	5.509	60			
		5.10	56				102	5.09	70
4.95	43			020	4.954	30			
4.37	100			201	4.383	85			
4.00	22			211	3.996	45			
				121	3.959	13			
				112	3.719	25			
		3.63	32				110	3.65	40
3.27	21			221	3.281	17			
3.12	53	3.11	72	122	3.114	100	201	3.11	75
		3.07	100				113	3.08	100
2.99	16			311	3.002	45			
2.95	19	2.97	12	131	2.949	45	202	2.965	15
		2.88	8				006	2.861	30
				231	2.631	11			
2.56	45	2.55	20	132	2.546	50	204	2.542	30

\* strengite  $\text{FePO}_4 \cdot 7\text{H}_2\text{O}$  PDF No. 33-667

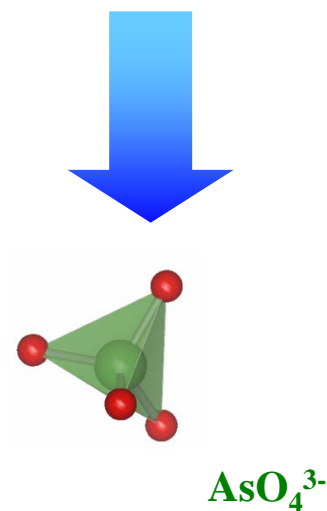
\*\* jarosite  $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$  PDF No. 22-827

# $\mu$ -XANES

As K-edge XANES spectra  
measured by 2 $\mu$ m X-ray beam

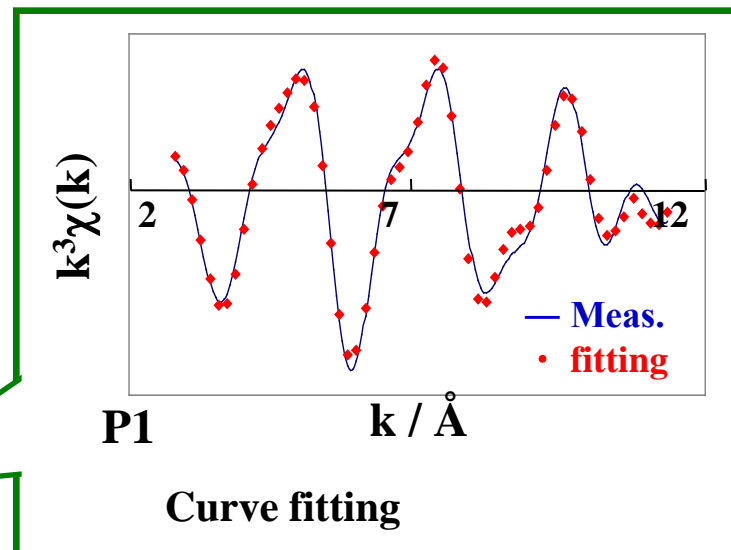
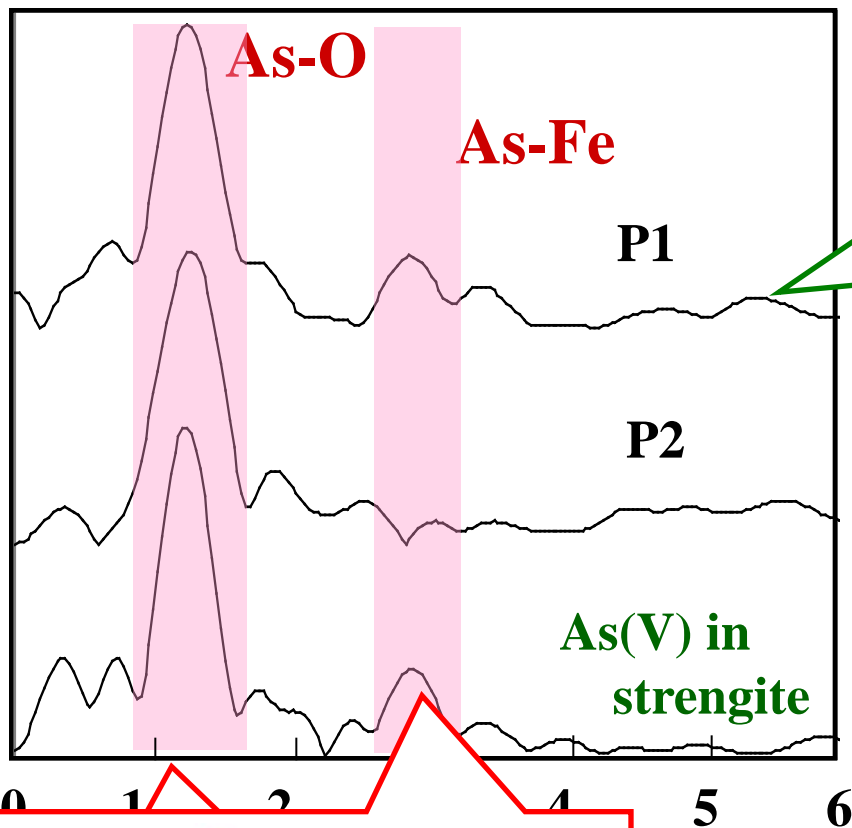


As exists as As(V) in the sample  
( $\text{AsO}_4^{3-}$ ,  $\text{HAsO}_4^{2-}$ )



strengite ( $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ )

# $\mu$ -EXAFS



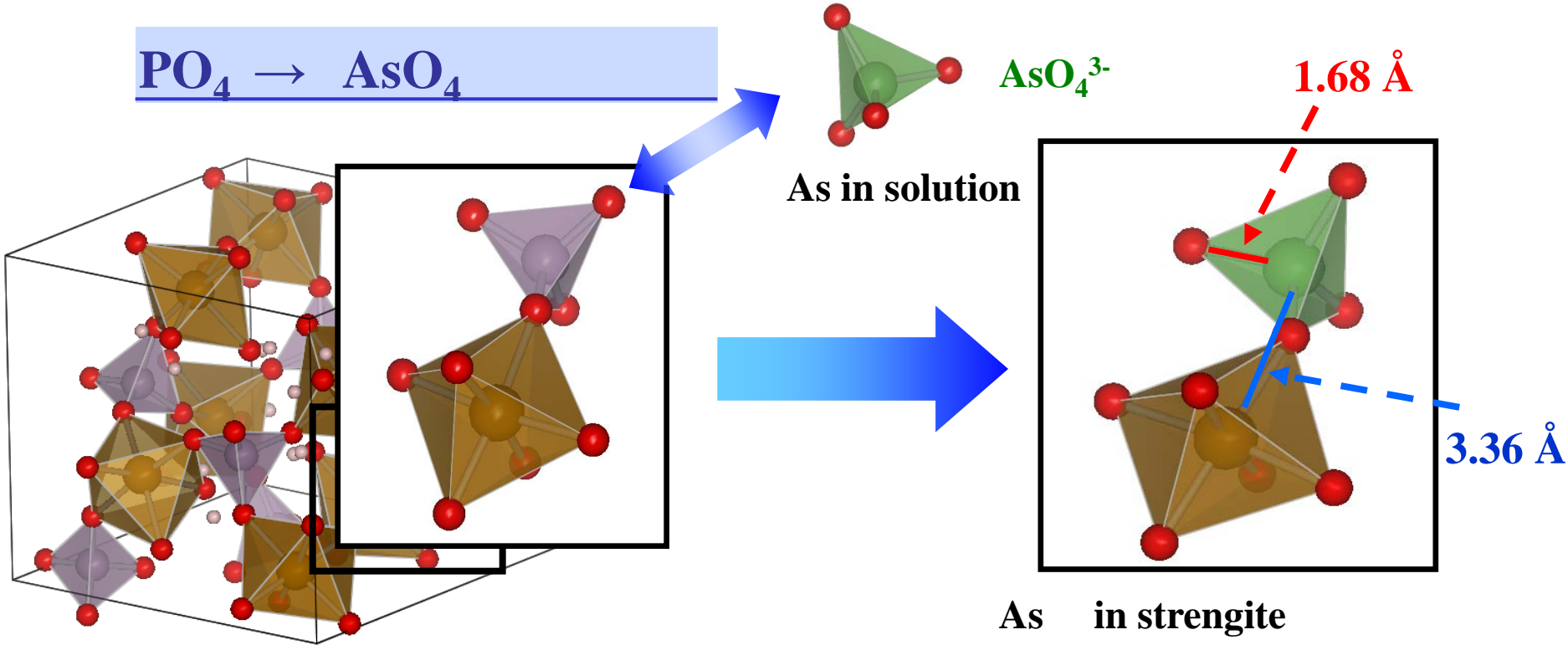
strengite  $\text{FePO}_4 \cdot 7\text{H}_2\text{O}$

EXAFS

	Atom	$r / \text{Å}$	CN
P1	O	1.68	4.0
	Fe	3.36	4.0
P2	O	1.69	4.0
As(V) in strengite	O	1.68	4.0
	Fe	3.35	4.0



# As accumulation mechanism



Crystal structure of strengite ( $FePO_4 \cdot 2H_2O$ )

Legend for the crystal structure diagram:

- $PO_4$  (purple tetrahedron)
- $AsO_4$  (green tetrahedron)
- $FeO_4(OH)_2$  Octahedron (brown octahedron)

Color key for atoms:

- O (red sphere)
- P (purple sphere)
- Fe (brown sphere)
- As (green sphere)

Substitution of  $PO_4$  tetrahedra in strengite ( $FePO_4 \cdot 2H_2O$ ) by  $AsO_4$  tetrahedra

# Conclusion

## Limitation of the SR-XRF

- . Microbeam analysis**
  - i) the thickness of the sample should be in the order of beam size**  
→ preparation of thin sample is not easy
  - ii) it takes long hours to carry out two dimensional mapping**  
because of large numbers of measurement points
- 2. Low excitation efficiency for light elements**
- 3. Special efforts is necessary to carry out quantitative analysis**
- 4. Sample damage should be considered if you use brilliant Undulator SR Source or white X-ray radiation. Especially, care must be taken about photo-reduction/oxidation of the component elements.**

# Attractiveness of (SR)-XRF

1. **Nondestructive analysis, multielemental analysis**

2. **Two dimensional resolution**

3. **Easy to carry out the analysis and easy to understand the results**

4. **Basic optical system for EDS analysis is simple**

**SR → Monochromator → sample → detector**

5. **We can analyze almost any samples**

**size → from cell level to sculpture, paintings**

**in situ, in vivo, in air at any temperature**

6. **Information**

**concentration: major (%), minor, trace (ppm) elements C ~ Na ~ U**

**distribution: from nm level to cm level**

**chemical state ( oxidation state, local structure) C ~ Si ~ U**

7. **Multiple SR-X-ray analysis: combination with X-ray diffraction and XAFS**