SR excited X-ray Fluorescence Analysis (SRXRF)

- Principles of SRXRF
- Micro-beam Analysis
- Applications of SRXRF

17 Sept., 2007
Cheiron School
Atsuo IIDA
Photon Factory
XRF Primer

Cheiron School 2007 by AOFSRR
A.Iida (PF)
X-ray Fluorescence Analysis

Excitation sources | Analytical techniques
--- | ---
X-rays | XRF (X-ray fluorescence analysis)
Electron | EPMA (Electron probe micro analyzer)
Charged particle | PIXE (Particle/Proton Induced X-ray emission)
X-ray Emission by Proton, Electron and Photon Excitation

3MeV Proton PIXE

Electron

Photon XRF

after C.J. Spaks, Jr
In “Synchrotron Radiation Research” (1980)
Energy Dispersive Mode vs. Wavelength Dispersive Mode

<table>
<thead>
<tr>
<th>Advantage</th>
<th>Energy Dispersive Mode</th>
<th>Wavelength Dispersive Mode</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>• High Efficiency</td>
<td>• High resolution</td>
</tr>
<tr>
<td></td>
<td>• Multi-elemental detection</td>
<td>• High S/B</td>
</tr>
<tr>
<td>Disadvantage</td>
<td>• Low resolution</td>
<td>• Low efficiency</td>
</tr>
<tr>
<td></td>
<td>• Scattering background</td>
<td></td>
</tr>
</tbody>
</table>

- Energy Dispersive
  - SR
  - Si(Li) detector
  - Ge / SDD

- Wavelength Dispersive
  - SR
  - Analyzer Crystal
  - Detector
  - Fluorescent X-rays
SRXRF Pond Sediment

Energy Dispersive Mode

Fe 6%, Br 17ppm, Zn 343 ppm
Total integrated fluorescence intensity by monochromatic excitation

\[ P_i(\lambda) = q \cdot E_i \cdot C_i \cdot \left\{ 1 - \exp(-\rho \cdot h \cdot A) \right\} \frac{\mu_{i\lambda} \cdot I_{\lambda} \cdot d\lambda}{A \cdot \sin \alpha} \]

\[ E_i = \frac{\gamma_K - 1}{\gamma_K} \cdot \omega_K \cdot g_{K\alpha} \]

\[ A = \frac{\mu_{s,\lambda}}{\sin \alpha} + \frac{\mu_{s,\lambda i}}{\sin \beta} \]

Thick Specimen ( \( h \rightarrow \infty \))

\[ I_{i,s}(\lambda) = q \cdot E_i \cdot C_i \cdot \frac{\mu_{i\lambda} \cdot U_{\lambda}}{A \cdot \sin \alpha} \]

Thin Specimen ( \( h \rightarrow 0 \))

\[ I_{i,s}(\lambda) = q \cdot E_i \cdot C_i \cdot \rho \cdot h \cdot \frac{\mu_{i\lambda} \cdot U_{\lambda}}{\sin \alpha} \]

\( C_i \): Concentration \hspace{1cm} \( h \): Thickness
Analytical calibration curve

- The relation of the measured values (x) to the concentration (c) (or any quantity(q)) of the material.
- \( x = g(c) \) or \( x = g(q) \)

- **Sensitivity** \( S \)
  - the increment of the measured value \( \Delta x \) for the unit change of the concentration \( \Delta c \).
  \[
  S = \frac{dx}{dc}
  \]

- **Limit of detection / minimum detection limit** \( c_L (q_L) \)
  - the minimum concentration of the analyte element or minimum quantity which can be measured

\[
\begin{align*}
  x_L &= \bar{x}_b + k \cdot s_b \\
  C_L &= \frac{x_L - \bar{x}_b}{S} \\
  \bar{x}_b &\quad \text{Average value for the blank} \\
  S_b &\quad \text{Standard deviation for the blank} \\
  k &\quad \text{Empirical value (}=3) \\
\end{align*}
\]
MDL (Minimum detection limit)

Minimum detection limit (MDL) \[ k = \frac{3C \sqrt{N_B}}{N_p - N_B} \]

Minimum quantification limit (MQL) \( (2k \sim 3.3k) \)
SR XRF

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A.Iida (PF)
Synchrotron radiation excited XRF
-SRXRF-

Advantages of conventional XRF

- Nondestructive
- Wide dynamic range
  major ~ trace
- User-friendly instruments
- Multi-elemental analysis
- High accuracy
- Easy to analyze

Advantages of SRXRF

- High sensitivity
  ng=>fg, ppm=>ppb
- Chemical state analysis
- Micro-beam analysis
  mm => μm
- Total reflection analysis
  $10^{15}$ atoms/cm$^2$
  => $10^8$ atoms/cm$^2$
### 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° 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 |
Monochromatic SR Excitation advantages: High Signal / Background ratio

(Sample: Chelete resin beads)

Monochromatic SR excitation

Laboratory source (2ndary target)

Continuum SR excitation

Storage Ring

Background Suppression due to the linearly polarized SR

\[ I \propto \sin^2 \Phi \]
Selective Excitation:
Resolving overlapping peaks: PbLα vs. As Kα Case

As K edge < PbL3 edge < $E_0$

As K edge < $E_0$ < PbL3 edge

Both As K and Pb L are excited.

As K series alone is excited. => As quantification becomes possible.
Hard X-ray Advantage: Heavy elements analysis

- Disadvantage of L series analysis
  - Complicated lines L$\alpha$, L$\beta$, L$\gamma$, L$l$, L$s$
  - Peak overlapping between L and K series lines

- Advantage of K series analysis
  - Simple line Structure K$\alpha$, K$\beta$
  - High sensitivity
  - Low absorption (bulk analysis)

High Energy 3rd generation ring
Wavelength shifter (Wiggler)
High Energy XRF

I. Nakai, Y. Terada et al. SPring-8 BL08W

=> forensic science (differentiation of origins)
Light Elements Analysis

• Light elements (C, N, O, Na~Ca)
  - biological system
    / material science

• low fluorescence yield
• strong absorption

Chlorella (NIES CRM #3)

[Graphs showing energy vs. intensity for different elements]

Soft X-ray Excitation from Undulator radiation

Excitation Efficiency is greatly enhanced.
Wavelength Dispersive XRF

**Wavelength Dispersive**

- High resolution (ca. 5 eV~ 50eV eV)
- High S/B

**Disadvantage**
- Low efficiency
- Scattering background

<table>
<thead>
<tr>
<th>Advantage</th>
<th>Wavelength Dispersive</th>
<th>Energy Dispersive</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>• High resolution (ca. 5 eV~ 50eV eV)</td>
<td>• High Efficiency</td>
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<td>• High S/B</td>
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<table>
<thead>
<tr>
<th>Disadvantage</th>
<th>Wavelength Dispersive</th>
<th>Energy Dispersive</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>• Low efficiency</td>
<td>• Low resolution (130 eV)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Scattering background</td>
</tr>
</tbody>
</table>
Wavelength Dispersive Technique

Multi-elemental geometry

θ-2θ geometry

Focusing geometry

Barrel type Crystal for 2D focusing
Wavelength Dispersive XRF Spectrum

Focusing geometry
Johansson, R=5"
LiF (200)
Grazing Incidence Condition
(High Brilliance Source)

- TXRF total reflection XRF
  - Ultra trace element analysis
- Depth analysis of a single thin layer or a multi-layer
- Reflectometry
TXRF for Ultra Trace Element Analysis

12.3KeV Si

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$^2$ => $10^8$ atoms/cm$^2$
TXRF with Wavelength Dispersive Analyzer

WD-TXRF spectra for trace elements (Ni, Co and Fe, 20 ppb each) in a micro drop (0.1 micro litter).

MDL 2~4fg
$10^7$ atoms/cm$^2$

@ SPring-8 BL40XU
Ge(220) Johansson focusing type WDXRF

K.Sakurai
SPring-8 Information
vol.6 No.1(2001)p.35
X-Ray Surface Analysis using GI Condition

Grazing Incidence condition

Diffraction/Scattering (GID/ GIS)
  - Structure Analysis
  - Reflectometry
      - Single
      - Poly

Spectroscopy
  - XRF
  - XAFS
  - XPS
      - Trace Analysis
      - Depth Analysis

Reciprocity Theorem

Grazing Exit condition

GE-XRF

X-ray Standing Wave
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 Kα and Kβ
  - Emission Spectroscopy
    - Resonant inelastic emission spectroscopy
    - .....
**XAFS (X-ray Absorption Fine Structure)**

- **Sample:** Crystal / amorphous materials

**XANES**
(X-ray Absorption Near Edge Structure)
- Electronic state
- Chemical state

**EXAFS**
(Extended X-ray Absorption Fine Structure)
- Local structure
- Coordination number

- Incident X-rays → Transmitted X-rays
- Fluorescent X-rays
- Secondary electrons

- Incident X-rays
- Cu FOIL 80 K
Chemical State analysis by XANES

"Chemical Shift of X-ray Absorption edge"

Fingerprint Method

K. Sakurai (NIMS)
Pre-edge energy analysis: Oxidation state analysis of transition elements

A linear relationship between pre-edge peak energy and iron oxidation state for oxide and silicate standards.

=> chemical state analysis of transition element in mineral and in the functional materials

Fe XANES for magnetite

Determination Fe3+/SFe ratio by the energy shift of a pre-edge in XANES
Micro-SR XRF

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A.Iida (PF)
**X-ray source and X-ray microbeam**

\[ \frac{1}{a} + \frac{1}{b} = \frac{1}{f} \quad M = \frac{b}{a} \]

Helmholtz invariant
\[ y \times u = y' \times u' \]

- \( y, y' \) source and focus size
- \( u, u' \) divergence and convergence angle

Low emittance source \( \Rightarrow \) 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

<table>
<thead>
<tr>
<th>Reflection</th>
<th>Grazing incidence mirror</th>
</tr>
</thead>
<tbody>
<tr>
<td>No chromatic aberration</td>
<td>spherical / aspherical</td>
</tr>
<tr>
<td></td>
<td>toroidal (bent cylinder)</td>
</tr>
<tr>
<td></td>
<td>elliptical, ellipsoidal</td>
</tr>
<tr>
<td></td>
<td>parabolic, paraboloidal</td>
</tr>
<tr>
<td></td>
<td>Capillary (single, poly)</td>
</tr>
<tr>
<td>Diffraction</td>
<td>Fresnel Zone plate</td>
</tr>
<tr>
<td>Energy dependence</td>
<td>Bragg-Fresnel lens</td>
</tr>
<tr>
<td></td>
<td>Crystal (asymmetric reflection / bent crystal)</td>
</tr>
<tr>
<td>Refraction</td>
<td>Compound refractive lens</td>
</tr>
</tbody>
</table>
X-ray microbeam Optics

Kirkpatrick-Baez optics

Ellipsoidal

Single tapered capillary

Bragg-Fresnel

Fresnel zone optics

Compound refractive optics
Fresnel Zone Plate Parameters

**Zone Plate Formulae**

\[ r_n^2 = n\lambda f + \frac{n^2\lambda^2}{4} \]  
(9.9)

\[ D = 4N\Delta r \]  
(9.13)

\[ f = \frac{4N(\Delta r)^2}{\lambda} \]  
(9.14)

\[ NA = \frac{\lambda}{2\Delta r} \]  
(9.15)

\[ F^# = \Delta r/\lambda \]  
(9.16)

Rayleigh res. = \[ \frac{0.610\lambda}{NA} = 1.22\Delta r \]  
(9.47, 9.48)

**DOF** = \[ \pm \frac{1}{2} \frac{\lambda}{(NA)^2} = \pm \frac{2(\Delta r)^2}{\lambda} \]  
(9.50, 9.51)

\[ \frac{\Delta \lambda}{\lambda} \leq \frac{1}{N} \]  
(9.52)

**Pinhole Formula**

\[ \theta_{null} = 1.22\lambda/d \]  
(9.36)

\[ \Delta r: \text{outermost zone width} \]
\[ N: \text{total number of zones} \]
\[ D: \text{lens diameter} \]
\[ \text{DOF: Depth of Focus} \]
\[ \Delta \lambda/\lambda: \text{maximum spectral bandwidth} \]

After D. Attwood “SX & EUV Radiation”
Grazing Incidence Optics

X-ray reflectivity for SiO$_2$ substrate

Glancing angle dependence for 8 keV X-rays ($\theta_c$=3.8 mrad).

Energy dependence for the glancing angle of 2.3 mrad ($E_c$=13 keV).

For reflectivity calculation, visit (CXRO) http://henke.lbl.gov/optical_constants/
Aberration of Grazing Incidence Mirror

Aberration
- Astigmatism
- Spherical aberration
- Coma
- Chromatic aberration

EX. Spherical mirror \( \frac{1}{u} + \frac{1}{v} = \frac{1}{f} \)
- Meridian focal length \( f_m = R \sin \theta_i / 2 \)
- Sagittal focal length \( f_s = R / 2 \sin \theta_i \Rightarrow f_m / f_s = \theta_i^2 \)

**Astigmatism**
- \( f_s \gg f_m \)
- \( R_s = R_m \sin^2 \theta_i \) toroidal mirror (bent cylinder)
  - Kirkpatrick-Baez optics

**Spherical aberration**
- Elliptical / ellipsoidal mirror
Elliptical Mirror technology

- ESRF
- Flexture Hinge

- APS Leaf spring
- APS GeoSoilEnvironCARS

- Xradia
- KB-SR1
Ultra High precision KB mirror
48 x 36nm (VxH)

By Osaka.U & SPring-8

Elastic Emission Machining
+ Chemical Vaporization Machining

FIG. 1. Optical system using KB mirrors.

S.Matsuyama et al. RSI 77(2006)093107

FIG. 9. Two-dimensional intensity profiles experimentally obtained, where scanning pitch is 10 nm. (a) Vertical focusing. (b) Horizontal focusing.
Conical Capillary (tapered capillary)

Fig III.7. Conical capillary geometry (from paper V).

After P. Engstrom
Hard x-ray nanoprobe based on refractive x-ray lenses

C.G. Schroer et al. APL 87(‘05)124103  @ ESRF ID13
X-ray Fluorescence imaging of single cells

- **K**: ~1%
- **Fe**: 76 ppm
- **I**: 580 ppm

A freeze-dried cancer cell treated with 5 µM of iodo-deoxydoxorubicin (anti-cancer drug).

- 14 keV polychromatic pink excitation
- CRL 60 x 60 µm², µg/cm²

S. Bohic et al. APL 78(01)3544
**Human Hair Analysis**

Synchrotron X-ray Microprobe

Cross section of hair shaft, 20mm from root end

51 x 51 step
3μm/step

Optical micrograph
SRXRF Perspective

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A. Iida (PF)
**SRXRF perspective**

- **Microbeam analysis**
  - Toward 10nm microbeam
  - Analytical SR microprobe
  - Novel Application

- **XRF imaging**
  - Micro-beam
  - Projection type
  - Micro-CT

- **Wavelength Dispersive**
  - Spectroscopy $=>$ Spectrometry
    - (RIXS, MCD ….)

- **Total reflection XRF**
  - $10^8$ atoms/cm$^2$ $=>$ $10^6$ atoms/cm$^2$
SRXRF perspective

Analytical SR Microprobe
- Multi-detection SR microprobe -

μ-SRXRF

<table>
<thead>
<tr>
<th>Chemical State</th>
<th>μ-XAFS</th>
</tr>
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<tr>
<td></td>
<td>X-ray Emission</td>
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<table>
<thead>
<tr>
<th>Local Structure</th>
<th>μ-XAFS</th>
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<tr>
<td></td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Crystal Structure</th>
<th>μ-XRD</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Poly- &amp; Single crystal</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Morphology</th>
<th>Imaging (absorption, fluorescence, phase)</th>
</tr>
</thead>
</table>
Analytical SR Microprobe
Center for nanoscale materials @APS
SR Microprobe ESRF ID22

Fig. 2 Overview of the vacuum vessel and equipments of the scanning X-ray microscope of ID21.
SRXRF Imaging

- $\mu$-beam Scanning
- Projection
- 3-dimensional (lateral + depth)
- Computed Tomograph
Full-Field X-ray Fluorescence Imaging Microscope with a Wolter Mirror (1)

M.Hoshino et al. 9th SRI
(a) X-ray fluorescence image of an alfalfa seed. Exp: 5 m × 12 integration. Bar: 0.5 mm. (CCD-2).
X-ray fluorescence energy spectra measured at (b) the luminous point and (c) the embryo. Exp: 100 s.
Quick Projection-type XRF imaging (1)

Advantages
• Large area (~cm²)
• Quick (0.1s)
• Medium spatial resolution (<20μm)

Collimator: Selection of Parallel beam

Grazing incidence: Large area imaging

Elemental sensitivity:
Scanning the excitation energy of incident X-rays

Quick Projection-type XRF imaging (2)

Electrodeposition from the mixed electrolyte of 0.25 mol/L CuSO$_4$ and 0.18 mol/L ZnSO$_4$ with 2.5 V applied voltage. Exposure time for each image is 1 min and image size is 12 × 12 mm$^2$. 
Confocal μ-XRF - depth profiling / 3D analysis -

A micro-volume is defined by the overlap of the foci of both X-ray optics. Incident beam focusing can be achieved by
• Poly capillary
• Monocapillary
• CRL(refractive lens)
•...


Hasylab, Bessy II, CHESS..
μ-XRF depth profiling of a Mughal miniature (paint multilayer on paper)

A Mughal miniature MIK I 5004 (10) "Abdallah Zakhmi" of doubtful origin (stylistically dated to the 17th century).

A classical Mughal miniature MIK I 5004 (3) dated from the 18th century.

HgS / 2PbCO₃·Pb(OH)₂ / paper

BESSY II
B.Kanngiesser et al. Nucl. Instr. Methods B211(03)259
SRXRF related Research Fields

- Biology / Medical
- Materials Science
- Methods
- Archaeology / Cultural Heritage
- Geoscience
- Others
Environmental Science
Stardust Project
Archeology/cultural Heritage

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A.Iida (PF)
SRXRF Applications to Environmental Science

- Phytoremediation
- Aerosol Particles in Urban area
- Waste fly ash
- Uranium fuel from Chernobyl
Arsenic hyper accumulator I

The Chinese Ladder fern (*Pteris vittata*), is a highly efficient accumulator of arsenic (up to 2%).

L.Q. Ma et al. Nature **409**(01) 579

Where is a hyperaccumulated element stored? What is the mechanism of the hyper accumulation.

μ-XRF reveals the accumulation of As in leaf (pinna)

I. Nakai et al.
2-D X-ray Fluorescence Imaging of Cadmium Hyperaccumulating Plants

X-ray beam size, 3x3 μm²; scan step, 3 μm; measurement time, 0.5 s/pixel; image size, 59 x 226 pixels. Cd absorption edge: 26.7 keV
A. Hokura et al. Chem. Lett. 35(’06)1246  SPring-8 BL37XU
## Particulate Matter (Aerosol)

### Effect

- **Health effects**
  - Asthma, Lung cancer, Cardiovascular issues, and Premature death.
  - Depending on the size of the particle
    - *PM10*: lungs, *PM2.5*: tend to penetrate into the gas-exchange regions of the lung, particles smaller than 100 nm: cell membranes

- **Radiative forcing**
  (Global warming)
  “the uncertainties relating to aerosol radiative forcings remain large.” [IPCC](https://www.ipcc.ch)

### Most Polluted World Cities by PM

<table>
<thead>
<tr>
<th>Particulate matter, $\mu g/m^3$ (2004)</th>
<th>City</th>
</tr>
</thead>
<tbody>
<tr>
<td>169</td>
<td>Cairo, Egypt</td>
</tr>
<tr>
<td>150</td>
<td>Delhi, India</td>
</tr>
<tr>
<td>128</td>
<td>Kolkata, India (Calcutta)</td>
</tr>
<tr>
<td>125</td>
<td>Taiyuan, China</td>
</tr>
<tr>
<td>123</td>
<td>Chongqing, China</td>
</tr>
<tr>
<td>109</td>
<td>Kanpur, India</td>
</tr>
<tr>
<td>109</td>
<td>Lucknow, India</td>
</tr>
<tr>
<td>104</td>
<td>Jakarta, Indonesia</td>
</tr>
<tr>
<td>101</td>
<td>Shenyang, China</td>
</tr>
</tbody>
</table>

The most of them are densely populated metropolitan areas in developing countries ([Wikipedia](https://en.wikipedia.org/wiki/Particulate_matter)).

The primary cause the burning of fossil fuels by transportation and industrial sources.
Waste fly ash

Fly ash contains potentially toxic trace metals (Pb, Ni, Cu, Cd) in concentrated amounts.

Multi-technique X-ray microprobe
@ ESRF ID22
KB E<18keV
CRL E>15keV

SRN 16('03)No.3, p.40
The origin of individual PM2.5 particles in Shanghai air

PM 2.5 refers to tiny particles or droplets in the air that are 2.5 μm or less.

Fine particles PM2.5 lead to health effects and are a major cause of visibility impairment in the urban area contributing to acid rain.

X.Li et al.
NIM B260 (2007) 336
X-ray microscopy for characterisation of fuel particles

**Uranium fuel from Chernobyl (1986)**

During the explosion (West) UO$_2$-cores with surrounding layer of reduced U with low weathering rates. During the subsequent fire (North) UO$_2$-core with surrounding layers of oxidised U$_2$O$_5$/U$_3$O$_8$ with high weathering rates.

**West**

μ-CT

μ-CT μ-XRD μ-XANES

μ-XANES

West: reduced U

B. Salub et al. NIM A 467(2001)1249
Stardust Project
NASA’s Comet Sample Return Mission

The capture of comet dust within aerogel

The Stardust mission was launched into space in early February 1999. Its destination - Comet Wild 2; its mission, to capture cometary materials before returning to earth in 2006.
Stardust Project (NASA)

Stardust track in Aerogel

X-ray CT and XRF

@SPring-8
http://www.spring8.or.jp/ja/current_result/SPring8News/no_33
As many as 80 researchers involved!

REPORT

Elemental Compositions of Comet 81P/Wild 2 Samples Collected by Stardust

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Tristan Ferroir,9 Christine Floss,10 Ian A. Franchi,2 Zak Gainsforth,9 Jean-Paul Gallien,16
Phillippe Gillet,3 Patrick G. Grant,2 Giles A. Graham,9 Simon F. Green,17 Farinche Grossenbacher,9
Philipp R. Heck,17 Gregory F. Herzog,18 Peter Hoppe,17 Friedrich Höz,10 Joachim Math,7
Konstantin Ignatyev,7 Hope A. Ishii,7 Koen Janssens,9 David Jowiski,9 Anton T. Kearsley,21
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Matthew Neville,22 Dimitri A. Papanastasiou,28 Pierre Pianetta,29 William Rao,29
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Julie Sheffield-Parker,2 Alexandre Simonetti,29 Kona Simitsky,26 Christoph.-J. Snee,16
Frank J. Stedman,24 Thomas Stephan,21 Rhonda M. Stroud,22 Jean Susini,6 Yoshi Suzuki,3
Stephen R. Sutton,23 Susan Taylor,1 Nick Vaughan,25 Jill Trodhar,23 Peter Tsou,28
Akira Tsuji,25† Kentaro Usui,9 Bart Vekemans,26 Edward P. Vincend,26 Laszlo Vincele,16
Andrew J. Westphal,26 Penelope Wozniakiewicz,22 Ernst Zimmer,22 Michael E. Zolensky 19

As many as 80 researchers involved!

We measured the elemental compositions of material from 23 particles in aerogel and from
residue in seven craters in aluminum foil that was collected during passage of the Stardust spacecraft
through the coma of comet 81P/Wild 2. These particles are chemically heterogeneous
at the largest size scale analyzed (~180 m). The mean elemental composition of this Wild 2 material
is consistent with the CI meteorite composition, which is thought to represent the bulk composition of
the solar system, for the elements Mg, Si, Mn, Fe, and Ni to 35%, and for Ca and Ti to 60%. The elements
Cu, Zn, and Ga appear enriched in this Wild 2 material, which suggests that the CI meteorites may not
represent the solar system composition for these moderately volatile minor elements.

NASA's Stardust spacecraft collected dust particles from comet 81P/Wild 2, at an
encounter speed of ~6.1 km/s, in silica aerogel capture cells and in impact craters (J).
Analytical results from the aerogel and foil were combined to provide a more comprehensive
elemental analysis of the Wild 2 particles.
CI- and Fe-normalized mean composition

Summary
The mean elemental composition of this Wild 2 material is consistent with the CI meteorite composition, which is thought to represent the bulk composition of the solar system, for the elements Mg, Si, Mn, Fe, and Ni to 35%, and for Ca and Ti to 60%. The elements Cu, Zn, and Ga appear enriched in this Wild 2 material, which suggests that the CI meteorites may not represent the solar system composition for these moderately volatile minor elements.
SR in Archeology and Cultural Heritage

Materials studied

- Pigment, painting, parchment, textile: 34%
- Ceramic, glaze, glass: 33%
- Metal, corrosion: 16%
- Bone, teeth, hair: 3%

SR techniques used

- XRF: 35%
- XRD: 43%
- XAFS: 16%
- IR: 3%
- SAXS: 3%

By Mark Pollard (Univ. Oxford) '05
Egyptian Chemicals (cosmetics)

Cosmetic powders in 52 make-up containers @ the Louvre Museum
μ-XRF + μ-XRD @ESRF ID22

Origin of the materials
(crystal structure + impurity pattern)

Phase structure determination
using the Rietveld refinement

Pb$_3$(CO$_3$)$_2$(OH)$_2$
Hydrocerrusite

E.Dooryhee et al.
Rad. Phys. Chem. 71(04)863
μ-XRF depth profiling of a Mughal miniature (paint multilayer on paper)

a Mughal miniature MIK I 5004 (10) “Abdallah Zakhmi” of doubtful origin (stylistically dated to the 17th century).

a classical Mughal miniature MIK I 5004 (3) dated from the 18th century.

HgS / 2PbCO₃·Pb(OH)₂ / paper

BESSY II
B.Kanngiesser et al. Nucl. Instr. Methods B211(03)259
SRXRF perspective

- **Microbeam analysis**
  - Toward 10nm microbeam
  - Analytical SR microprobe
  - Novel Application
- **XRF imaging**
  - Micro-beam
  - Projection type
  - Micro-CT
- **Wavelength Dispersive**
  - Spectroscopy => Spectrometry
    (RIXS, MCD ….)
- **Total reflection XRF**
  - $10^8$ atoms/cm$^2$ => $10^6$ atoms/cm$^2$

If you have any questions about SRXRF please contact:
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