

Beamline 5-ID at NSLS-II – using X-rays for microscopy and spectroscopy

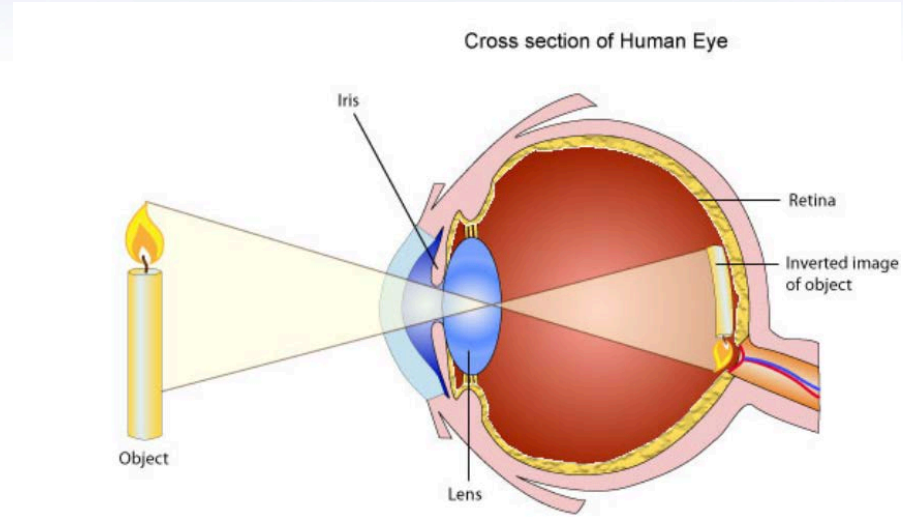
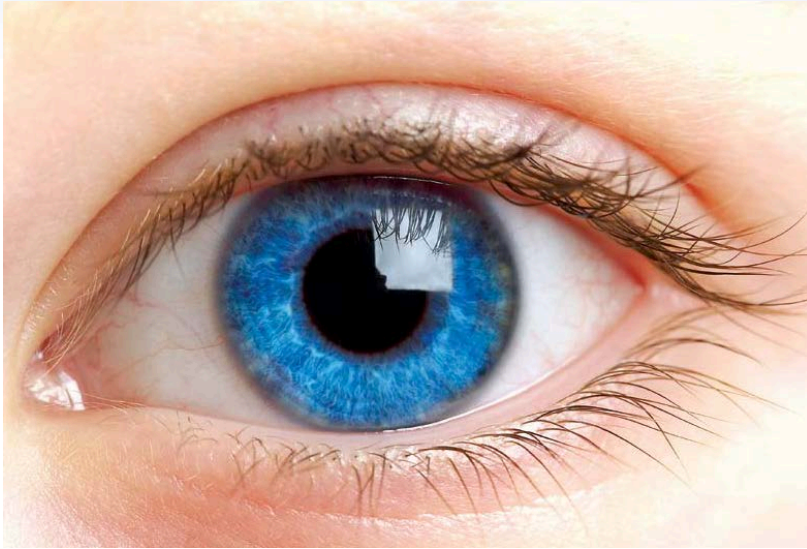
February 08, 2018

Juergen Thieme

Energy Sciences Directorate, Brookhaven National Laboratory



The smallest thing the human eye can see



Source: WWW

Rule of thumb:

The smallest thing the human eye can see is about the size of the human hair.

Size of the human hair:

Diameter 15-100 micrometer.

1 millimeter (mm) = 4/100 inch
1 micrometer (μm) = 1/100 mm
= 4/100000 inch

But what about the real small things?

Microscopy!

Optical microscopy using visible light

History



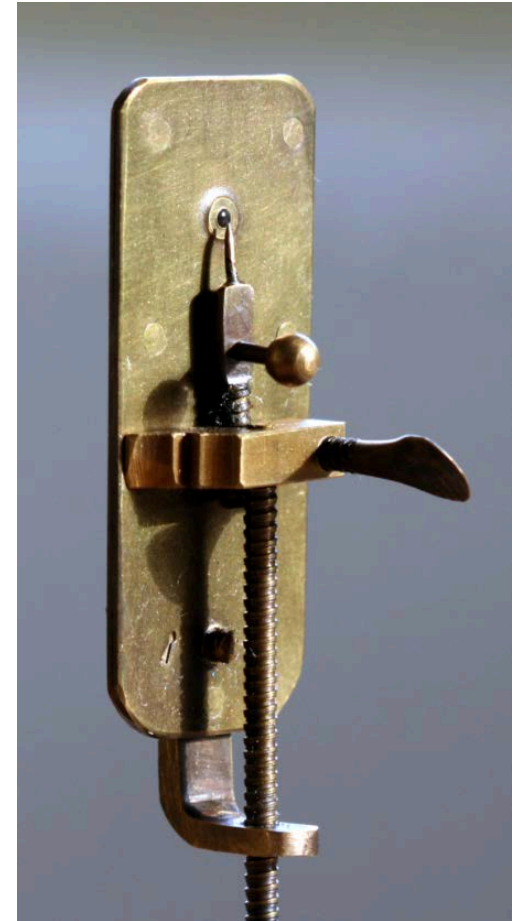
Antonie van Leeuwenhoek
(1632-1723)
“Father of Microbiology”

- Built many microscopes
- Made more than 500 lenses
- Magnification up to 150x

Discoveries

- Infusoria
- Bacteria
- Vacuoles in cells
- Spermatozoa

Height: 2 inch
One small lens
Tip for sample
Screws for adjustment



Source: WWW

Optical microscopy using visible light



Italian Compound
Tripod Microscope
(circa late 1600s)

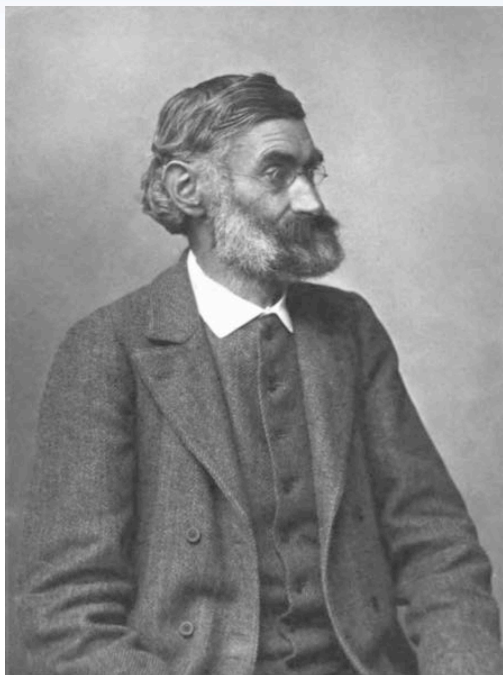
Source: WWW



Microscopes of the 18th century

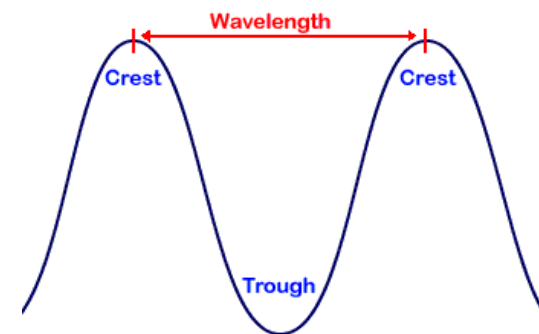
Scientists believed into the 19th century, the better the lenses the better the resolution, leading to atomic resolution.

The resolution of a microscope



Ernst Abbe
(1840-1905)

$$d_{min} = \frac{\lambda}{2}$$



In 1876 Abbe stated that there is no real chance to see finer structures than $0.2 \mu\text{m}$.

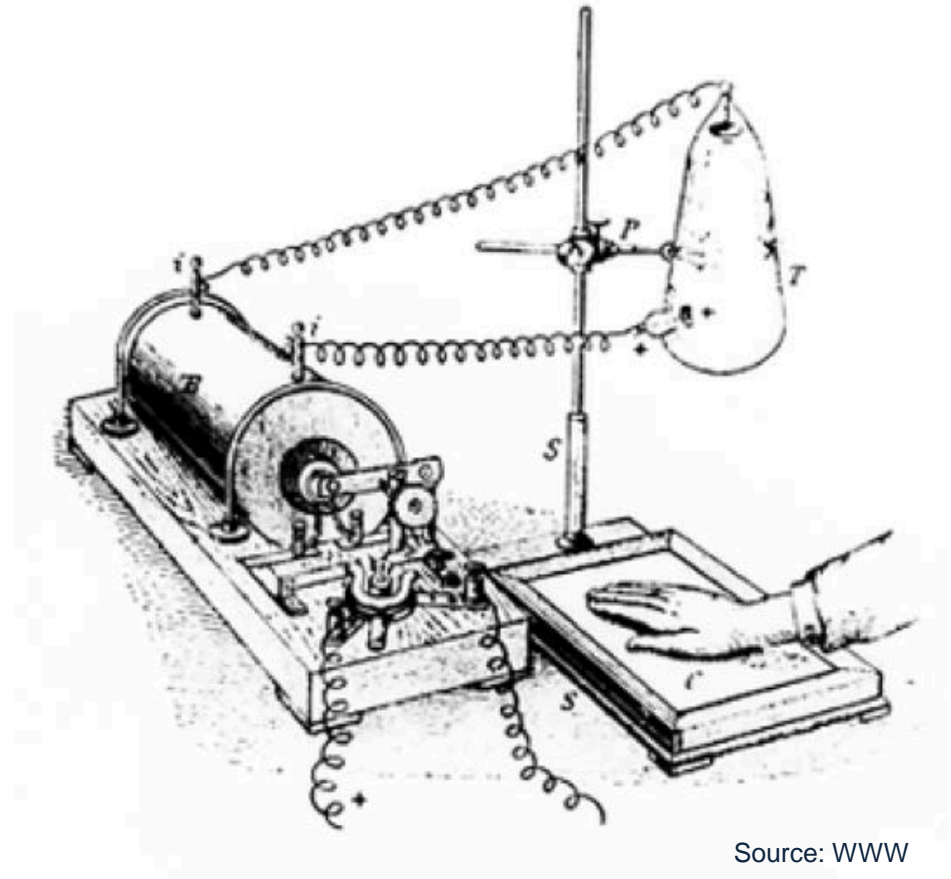
He added that there might be, however, unknown phenomena between heaven and earth we are not able to dream of.

The discovery of X-rays



Wilhelm Conrad Röntgen
(1845-1923)

Nov 8, 1895 Discovery of X-rays
1901 First Nobel Prize in Physics



Source: WWW

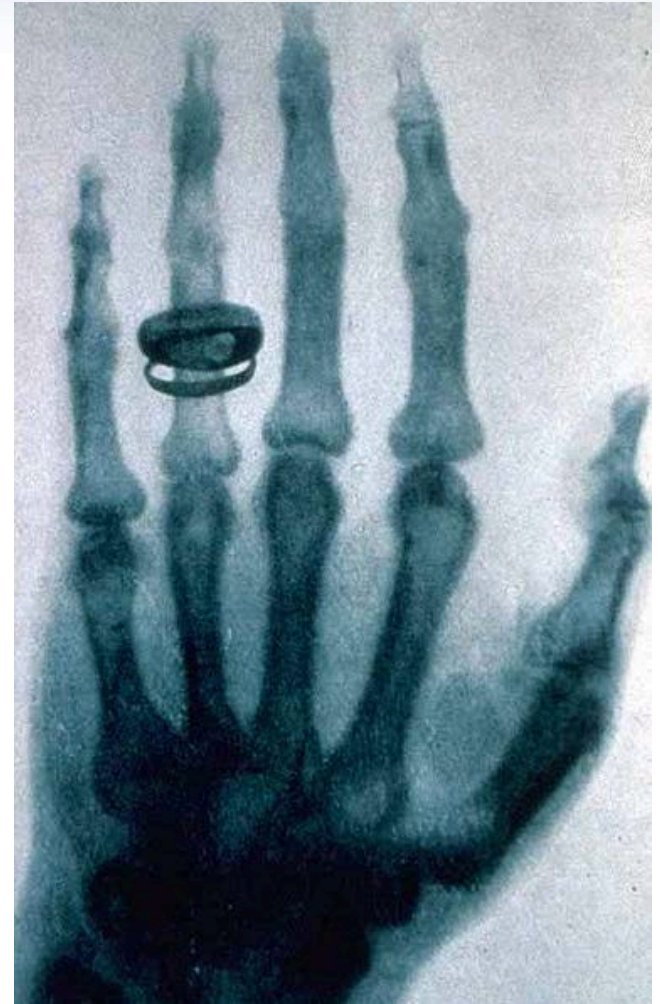
An excellent possibility to overcome the resolution limit is using X-rays, electromagnetic radiation of very short wavelength λ .

The discovery of X-rays



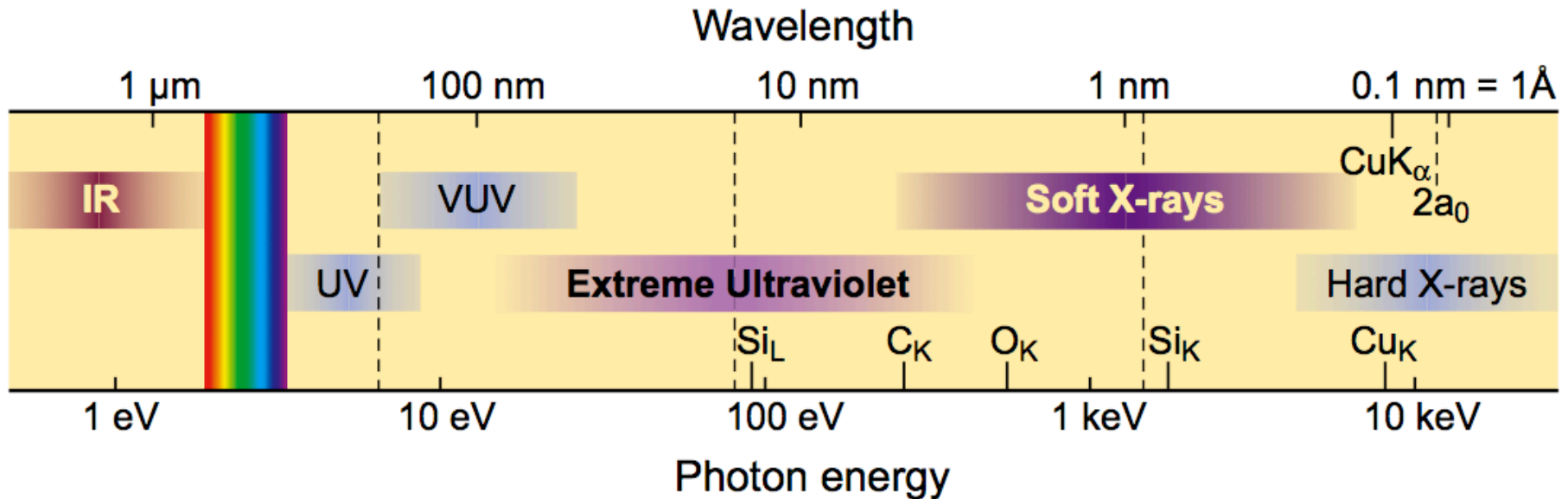
Dec 22, 1895
Hand of
Anna Röntgen

Jan 23, 1896
Hand of
von Kölliker



Source: WWW

X-radiation



Resolution in X-ray microscopes shown so far:

Limit at present defined by quality of the optical system.
Spatial resolution of around **5 nm** have been reported.

1 micrometer (μm) = 1/1000 mm = 40 millionth of an inch
1 nanometer (nm) = 1/1000 μm = 40 billionth of an inch
Example: Diameter of an atom ≈ 0.1 – 0.5 nanometer

Synchrotron radiation – an excellent way to create a brilliant X-ray beam



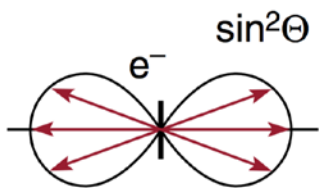
Dipole radiation

Heinrich Hertz
(1857-1894)

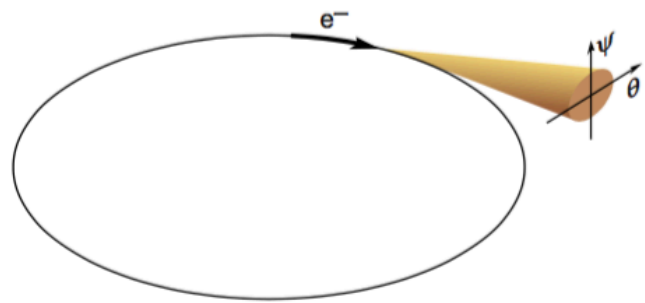
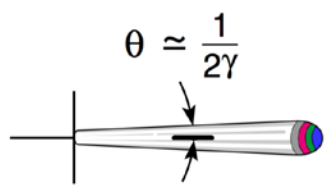
The key to modern science using X-rays

Accelerate an electron that has almost the speed of light, e.g. by forcing it on a bent path. The electron will emit light in a narrow cone in forward direction.
(Dmitri Iwanenko and Isaak Pomerantschuk, 1944)

Frame of Moving e^-

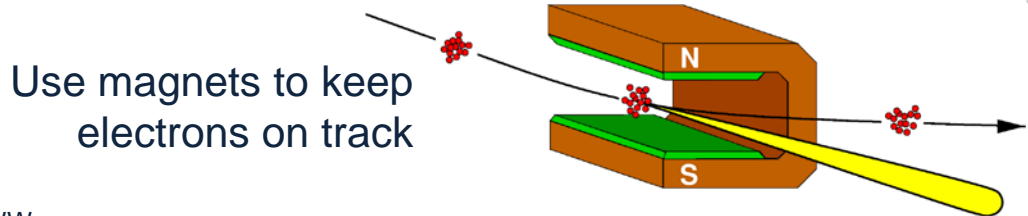


Frame of Observer



Synchrotron radiation

- 10^{10} brighter than the most powerful (compact) laboratory source
- An x-ray "light bulb" in that it radiates all "colors" (wavelengths, photons energies)



Use magnets to keep electrons on track

Source: WWW

How to build a synchrotron radiation facility

Injection system:

Emitting electrons, process is very similar to what happens on the tungsten filament of a light bulb.

Linear accelerator to bring electrons to a base speed.

Booster ring:

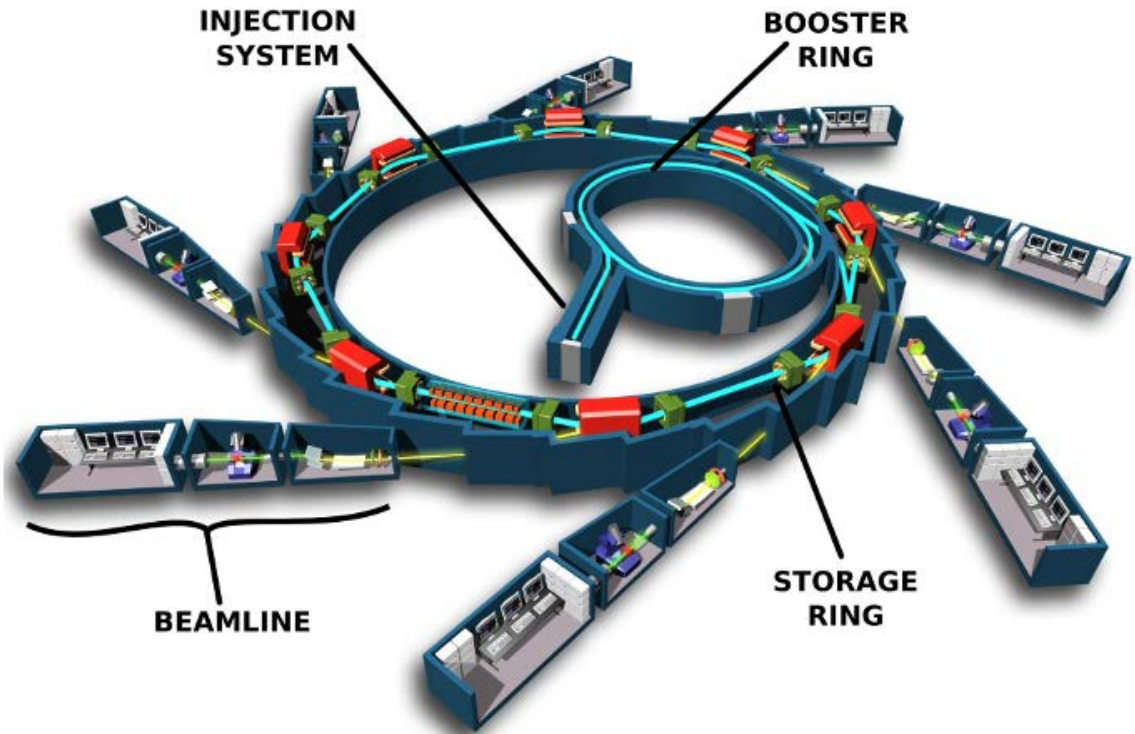
Accelerates the electrons to the final speed for which the storage ring is designed.

Storage ring:

Stores the electron current at a fixed energy / speed.

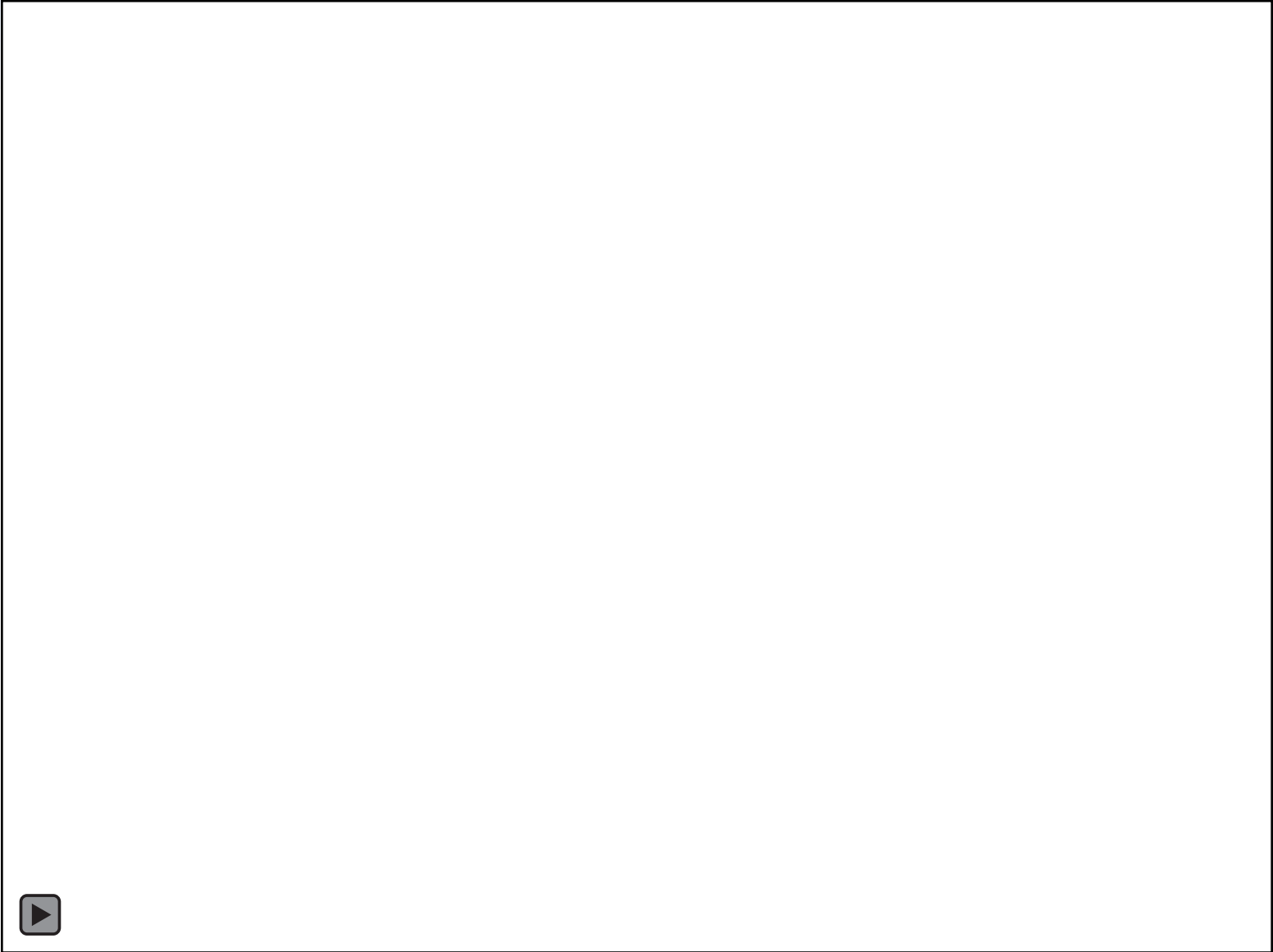
Beamlines:

The actual experimental stations.
Many different experiments at the same time possible.



National Synchrotron Light Source II:
Energy 3 GeV corresponds to about 99.996%
the speed of light.

Making Synchrotron Light



Synchrotron radiation facilities

Source: WWW



6 GeV: ESRF, Grenoble, France



7 GeV: APS, Chicago, IL



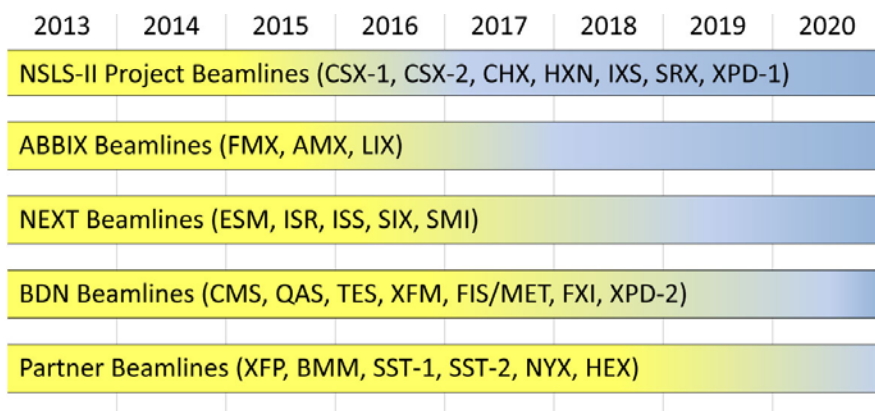
8 GeV: SPring-8, Hyogo, Japan



NSLS-II - One of the world's most advanced synchrotron light sources



- NSLS-II is a state-of-the-art, medium-energy electron storage ring (3 GeV) designed to deliver world-leading intensity and brightness, and produces x-rays more than **10,000 times brighter** than the original NSLS.
- Construction cost was **US \$ 912,000,000** (including initial project beamlines). Construction of NSLS-II began in 2009 and produced 'first-light' in 2014.

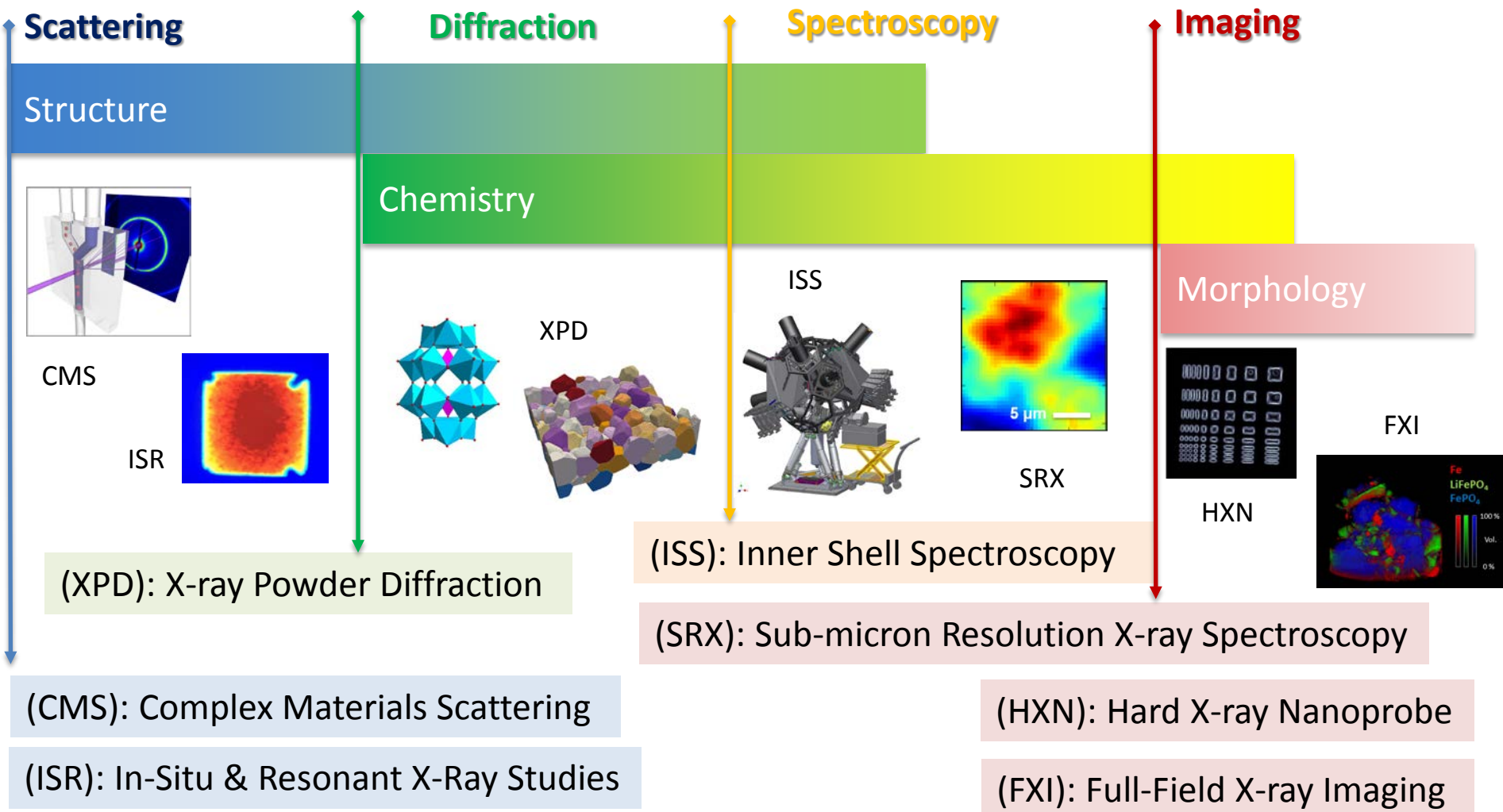


- When fully built out, National Synchrotron Light Source II will accommodate approximately **60 to 70 beamlines**. **30 beamlines** are currently in various stages of development and will provide significant research capacity in operations.

= Design/Construction = Operations

Highlights of NSLS-II Capabilities:

Suite of beamlines with complementary techniques - enabling time-resolved, *operando*, multi-modal and multi-dimensional studies

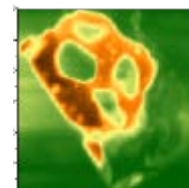
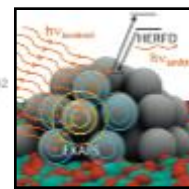
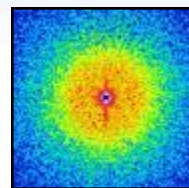
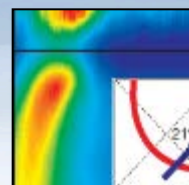
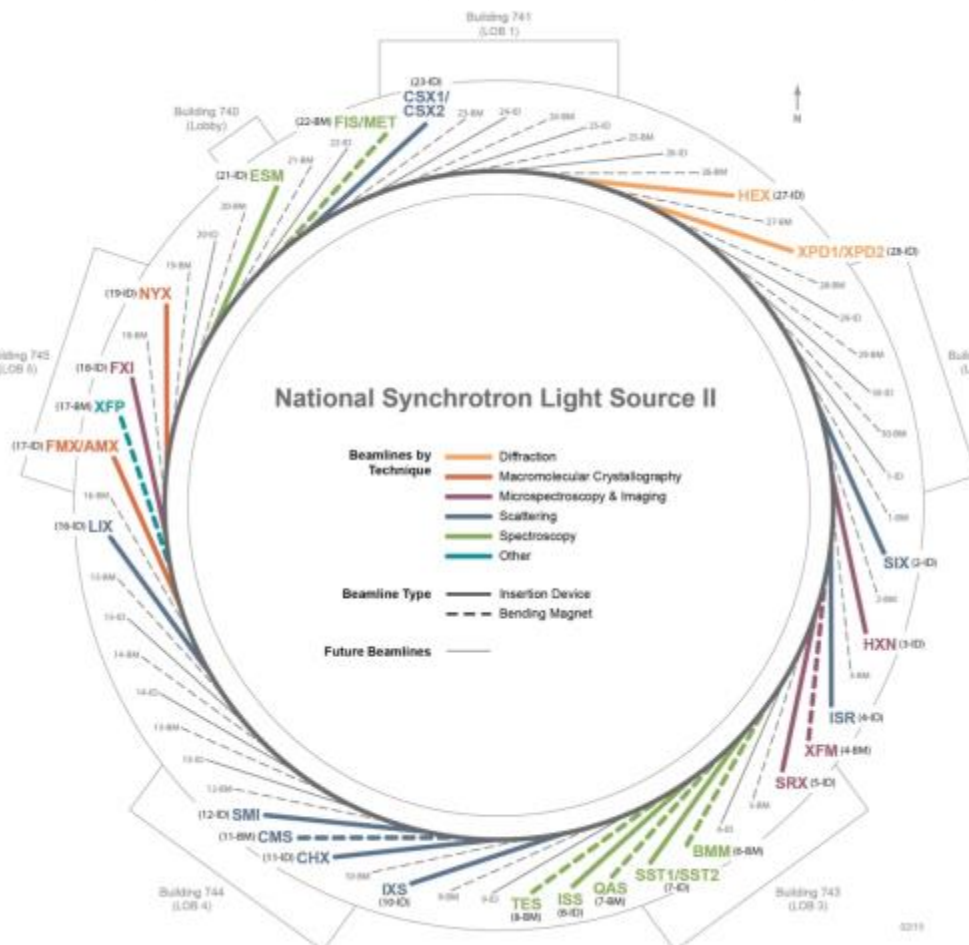


NSLS-II

Current Suite of Beamlines

- 19 Operating/Commissioning
- 10 Under Development

<http://www.bnl.gov/ps/nsls2/beamlines/map.php>



Soft X-Ray Scattering & Spectroscopy

- 23-ID-1: Coherent Soft X-ray Scattering (2015)
- 23-ID-2: Soft X-ray Spectro & Polarization (2015)
- 21-ID: Photoemission-Microscopy Facility (2016)
- 2-ID: Soft Inelastic X-ray Scattering (2017)
- 22-BM: Magneto, Ellips, High-P Infrared (2018)

Complex Scattering

- 10-ID: Inelastic X-ray Scattering (2015)
- 11-ID: Coherent Hard X-ray Scattering (2015)
- 11-BM: Complex Materials Scattering (2016)
- 12-ID: Soft Matter Interfaces (2016)

Diffraction & In Situ Scattering

- 28-ID-1: X-ray Powder Diffraction (2015)
- 28-ID-2: X-ray Powder Diffraction (2017)
- 4-ID: In-Situ & Resonant X-ray Studies (2016)
- 27-ID: High Energy X-ray Diffraction (2020)

Hard X-Ray Spectroscopy

- 8-ID: Inner Shell Spectroscopy (2016)
- 7-BM: Quick X-ray Absorption and Scat (2017)
- 8-BM: Tender X-ray Absorption Spectros (2016)
- 7-ID-1: Spectroscopy Soft and Tender (2017)
- 7-ID-2: Spectroscopy Soft and Tender (2017)
- 6-BM: Beamline for Mater. Measurement (2017)

Imaging & Microscopy

- 3-ID: Hard X-ray Nanoprobe (2015)
- 5-ID: Sub-micron Resolution X-ray Spectro (2015)
- 4-BM: X-ray Fluorescence Microscopy (2017)
- 18-ID: Full-Field X-ray Imaging (2018)

Structural Biology

- 17-ID-1: Frontier Macromolec Cryst (2016)
- 17-ID-2: Flexible Access MacromolCryst (2016)
- 16-ID: X-ray Scattering for Biology (2016)
- 17-BM: X-ray Footprinting (2016)
- 19-ID: Microdiffraction Beamline (2017)

The essential question



This is all nice and good and with NSLS-II the United States has built a worldwide leading synchrotron radiation facility,

but what is it good for?

Why did the American tax payer invest almost \$ 1b into such a facility?

**Fundamental
And Applied
Research**



Motivation 1: Do we need fundamental research?

Example: Gorilla Glas

developed by Corning in the 1960s
and it was not clear what to use it for.

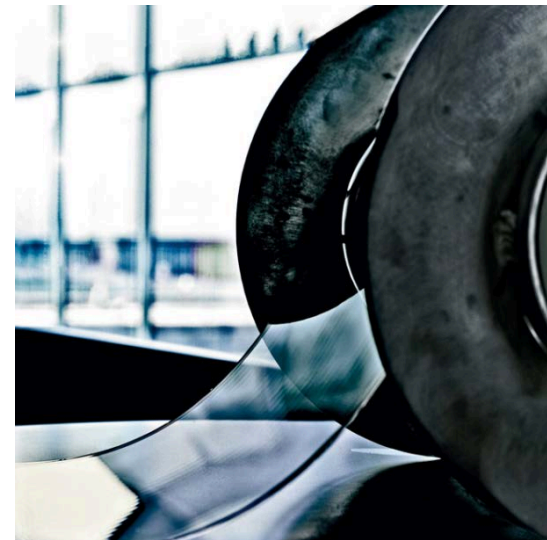
Steve Jobs approached Corning 2005 to find a glass
for Apple's iPhone.

It should be thin, light and hard to break.

Corning realized that their glass from the 60's was
exactly what Apple was looking for.

Now, more companies have developed similar
glass types, but 10 years ago, gorilla glass was it!

Modern, thin glass
on a spool.



Source: WWW

Motivation 2: Chemistry of small particles affects function of a large factory

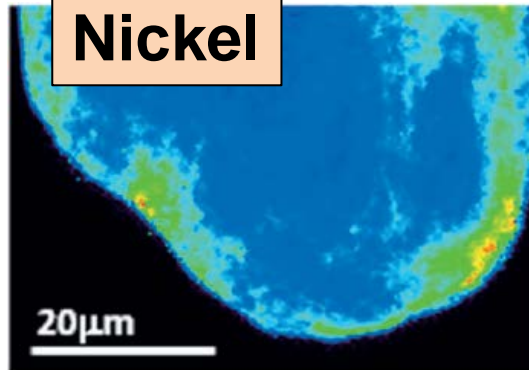
Reactor



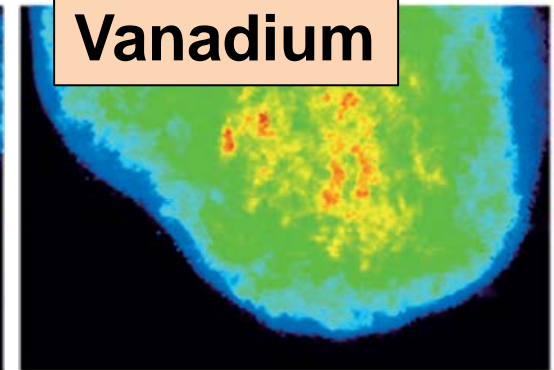
Oil industry uses Fluidized Catalytic Cracking: Converts crude oil to gasoline and other products. One of the most important conversion processes!

Catalysts are small particles, 10-100 μm in size, circulating between reactor and regenerator.

Nickel



Vanadium



Main Column

Regenerator

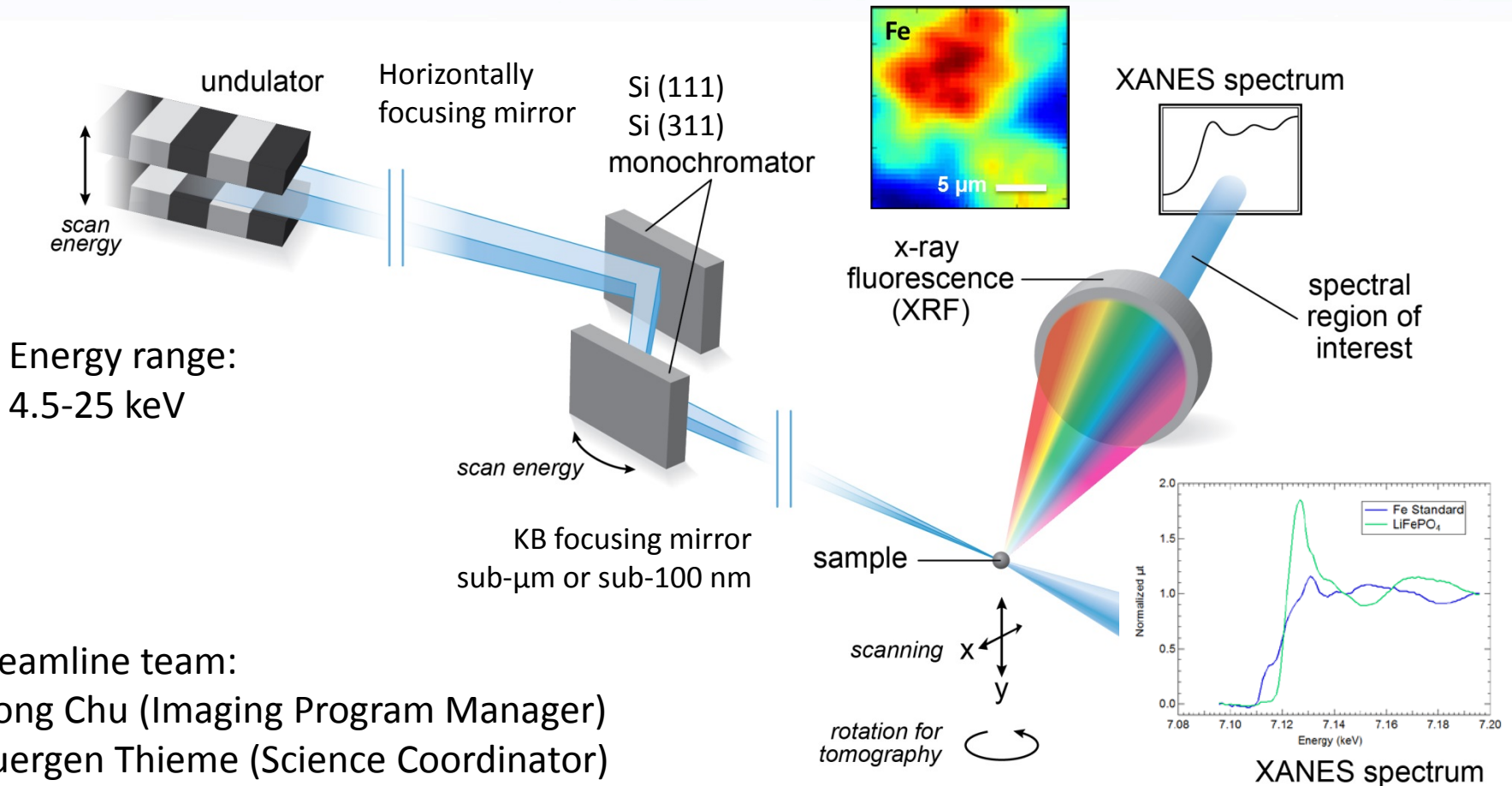
Problem: Nickel and vanadium from the crude oil accumulate over time on the catalyst and deteriorate the catalytic process.

Picture: Wikipedia

Wanted: X-ray spectroscopy with resolution below 1 μm .

Goal: Understand chemistry better and improve the process.

The sub-micron resolution X-ray spectroscopy beamline



<https://www.bnl.gov/ps/beamlines/beamline.php?b=SRX>

X-ray fluorescence spectromicroscopy at SRX

Elements for which X-ray spectroscopy with sub- μm spatial resolution is possible

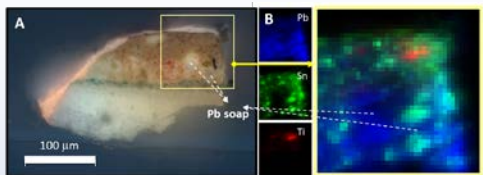
1 H hydrogen 1.008	2 He helium 4.003
3 Li lithium 6.941	4 Be beryllium 9.012
11 Na sodium 22.99	12 Mg magnesium 24.31
19 K potassium 39.10	20 Ca calcium 40.08
37 Rb rubidium 85.47	38 Sr strontium 87.62
55 Cs cesium 132.9	56 Ba barium 137.3
87 Fr francium 223	88 Ra radium 226

21 Sc scandium 44.96	22 Ti titanium 47.87	23 V vanadium 50.94	24 Cr chromium 52.00	25 Mn manganese 54.94	26 Fe iron 55.85	27 Co cobalt 58.93	28 Ni nickel 58.69	29 Cu copper 63.55	30 Zn zinc 65.41
39 Y yttrium 88.91	40 Zr zirconium 91.22	41 Nb niobium 92.91	42 Mo molybdenum 95.94	43 Tc technetium 98	44 Ru ruthenium 101.1	45 Rh rhodium 102.9	46 Pd palladium 106.4	47 Ag silver 107.9	48 Cd cadmium 112.4
71 Lu lutetium 175.0	72 Hf hafnium 178.5	73 Ta tantalum 180.9	74 W tungsten 183.8	75 Re rhenium 186.2	76 Os osmium 190.2	77 Ir iridium 192.2	78 Pt platinum 195.1	79 Au gold 197.0	80 Hg mercury 200.6
103 Lr lawrencium 262	104 Rf rutherfordium 261	105 Db dubnium 262	106 Sg seaborgium 266	107 Bh bohrium 264	108 Hs hassium 277	109 Mt meitnerium 268	110 Ds darmstadtium 281	111 Rg roentgenium 272	112 Cn copernicium 285

5 B boron 10.81	6 C carbon 12.01	7 N nitrogen 14.01	8 O oxygen 16.00	9 F fluorine 19.00	10 Ne neon 20.18
13 Al aluminum 26.98	14 Si silicon 28.09	15 P phosphorus 30.97	16 S sulfur 32.07	17 Cl chlorine 35.45	18 Ar argon 39.95
31 Ga gallium 69.72	32 Ge germanium 72.64	33 As arsenic 74.92	34 Se selenium 78.96	35 Br bromine 79.90	36 Kr krypton 83.80
49 In indium 114.8	50 Sn tin 118.7	51 Sb antimony 121.8	52 Te tellurium 127.6	53 I iodine 126.9	54 Xe xenon 131.3
81 Tl thallium 204.4	82 Pb lead 207.2	83 Bi bismuth 209.0	84 Po polonium 209	85 At astatine 210	86 Rn radon 222
113 Uut ununtrium 284	114 Fl flerovium 289	115 Uup ununpentium 288	116 Lv livermorium 292	117 Uus ununseptium 293	118 Uuo ununoctium 294

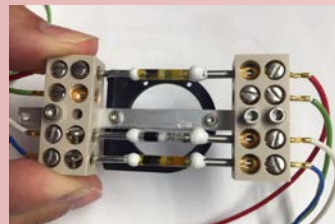
57 La lanthanum 138.9	58 Ce cerium 140.1	59 Pr praseodymium 140.9	60 Nd neodymium 144.2	61 Pm promethium 145	62 Sm samarium 150.4	63 Eu europium 152.0	64 Gd gadolinium 157.3	65 Tb terbium 158.9	66 Dy dysprosium 162.5	67 Ho holmium 164.9	68 Er erbium 167.3	69 Tm thulium 168.9	70 Yb ytterbium 173.0
89 Ac actinium 227	90 Th thorium 232.0	91 Pa protactinium 231.0	92 U uranium 238.0	93 Np neptunium 237	94 Pu plutonium 239	95 Am americium 243	96 Cm curium 247	97 Bk berkelium 247	98 Cf californium 251	99 Es einsteinium 252	100 Fm fermium 257	101 Md mendelevium 258	102 No nobelium 259

Art Conservation

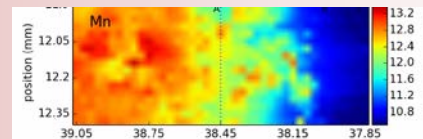


Pb-soap Formation

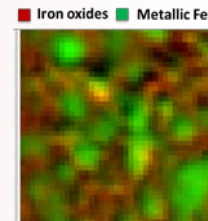
Novel Energy Storage Systems:



Li-S Battery

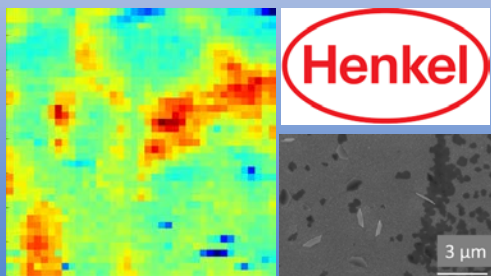


Aqueous Low-cost battery

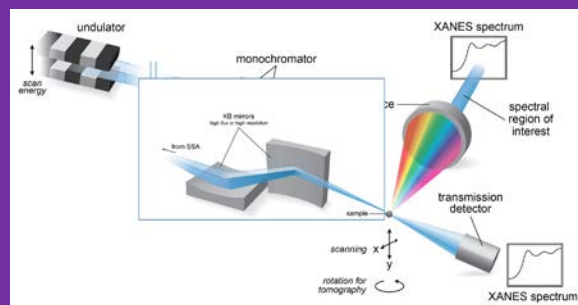


CNT additives

Industrial Application

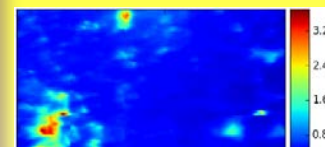


Heterogeneity In ZnO thin film

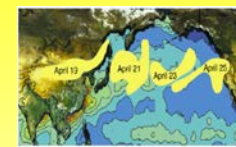


Sub-micron Resolution X-ray Spectroscopy (SRX) Beamline

Environment Science

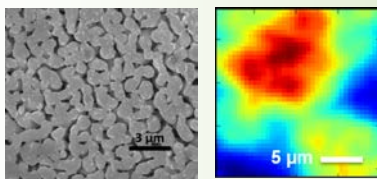


Soil Science



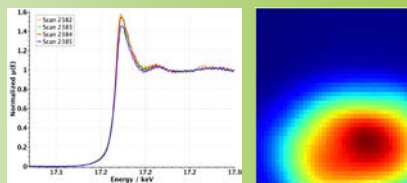
Aerosols

Materials Science



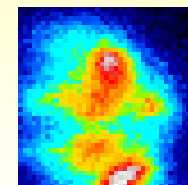
Nano-porous Materials

Nuclear Forensics



Uranium Chemical Analysis

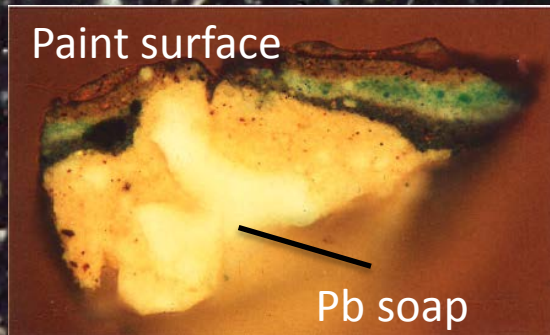
Biology



Subcellular element distribution

Art Conservation

Lead Soap Formation and Degradation in Painting



Pb 'soap' formation: A white aggregate of a lead containing compound 10 to 20 μm in size is visible in the ground layer as it starts to break through the paint layers.

Surface texture of rounded protrusions resulting from the formation of lead soaps in the ground layer as it aged

Images and Text are from The Metropolitan Museum of Art Bulletin, Summer 2009, article by S. Centeno and D. Mahon



John Singer Sargent (American, 1856-1925).
Madame X (Madame Pierre Gautreau), 1883-84.
Oil on canvas, 208.6 x 109.9 cm
The Metropolitan Museum of Art,
Arthur Hoppock Hearn Fund, 1916

Art conservation: prevention of soap formation

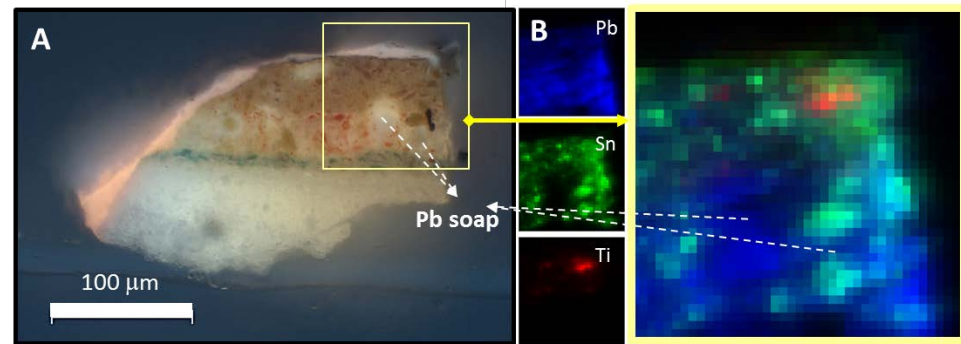
Chemical analysis on 15th century painting



Crucifixion And Last Judgment Diptych

Artist: Jan van Eyck (1390–1441)

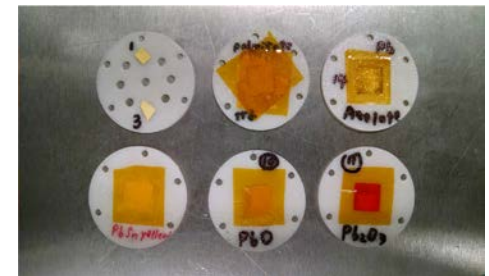
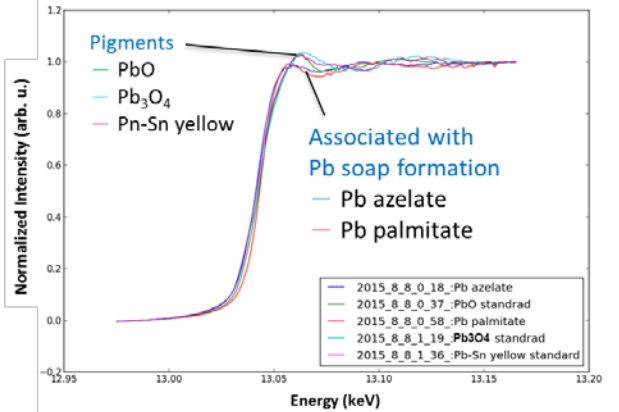
Date: ca. 1440–41



X-ray fluorescence mapping shows Pb & Sn segregation

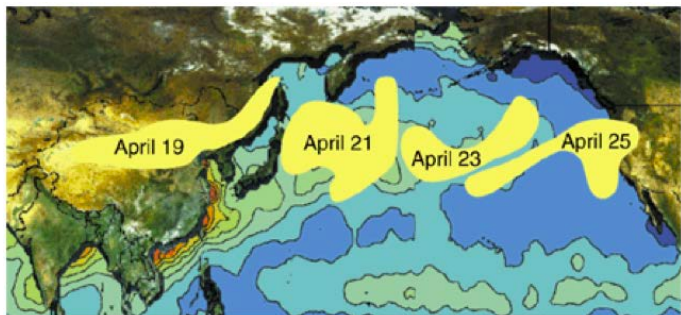
X-ray absorption spectroscopy: chemical speciation

Differentiate pigments from the degraded Pb soap compounds



Spatial Analysis of Metals within Individual Aerosol Particles Sampled from the Asian Continental Outflow

Goal: identify trace elemental content in single aerosol particles and assess impact on human health

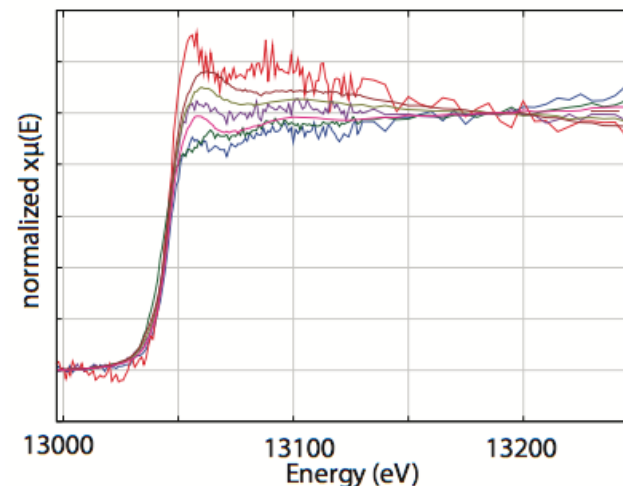
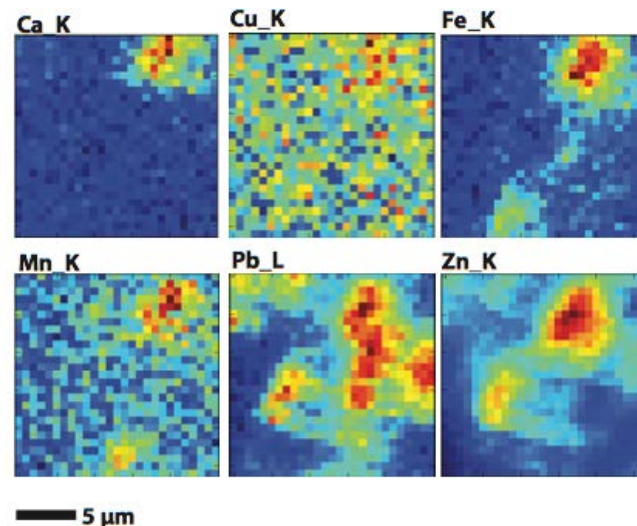


Aerosols are particles in air with sizes of just a few μm and can be transported over very long distances.

Aerosol samples have been studied using the SRX beamline, mapping the metal content in single particles and showing the correlations between the metals. Further analysis of the Pb XANES spectra promise to reveal additional details regarding Pb mineralogy which is important for judging their effects on human health.

(Ryan Moffet, University of the Pacific;
Martin Schoonen, BNL; et al.)

XRF images, taken in high-flux mode 25 x 25 μm , 0.5 μm step size showing correlations between metals



XANES spectrum of lead in the aerosol sample

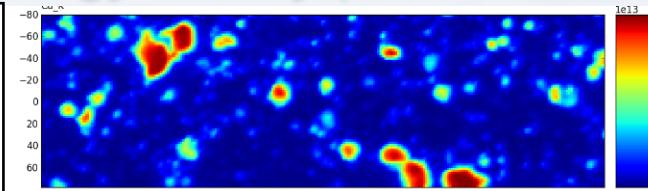
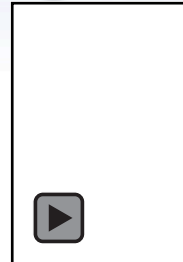
In Operando Studies on Future Energy Storage Materials

Li-S battery: Delivers significantly higher energy density (Gravimetric 6x)

Goal: Addressing the critical challenge in Li-S:
low conductivity of S cathode

→ improved by using **hybrid cathode: CuS-S**

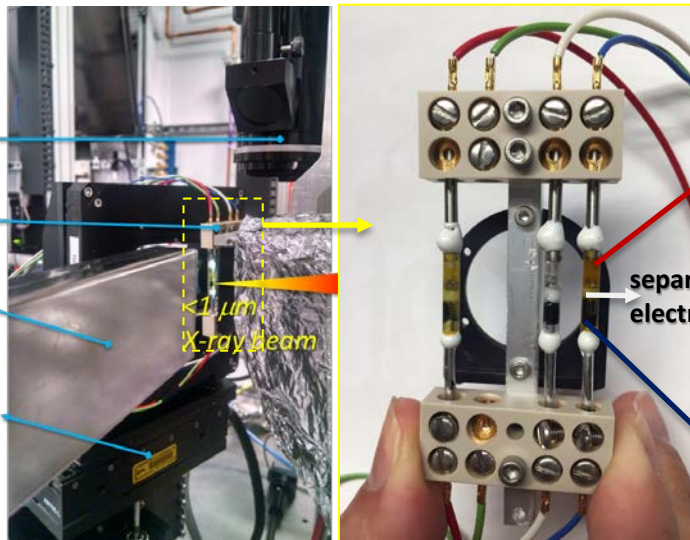
- Issues: dissolution of Cu & re-deposition



Cu mapping in Cu-S hybrid cathode

Step size:
2 μm
area:
520 x 80 μm^2

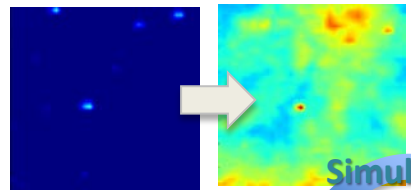
First time **direct visualization in operando**



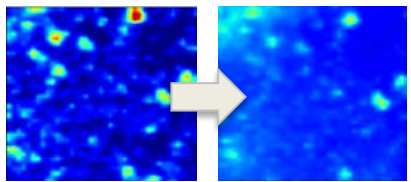
@Sub-micron Resolution X-ray Spectroscopy (SRX) Beamline

A. Elemental Distribution Evolution (XRF)

Anode: Re-deposition



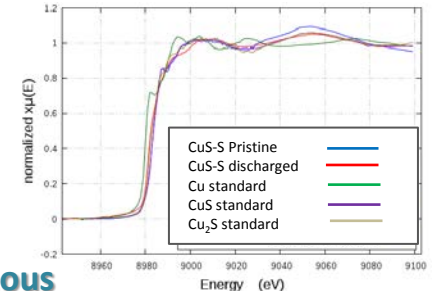
Cathode: Dissolution



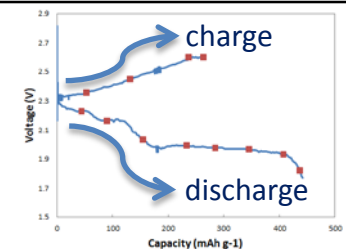
*Cu mapping
Pristine vs Discharged*

Simultaneous
Correlation

B. Chemical Evolution (XANES)



C. Electrochemical Evolution

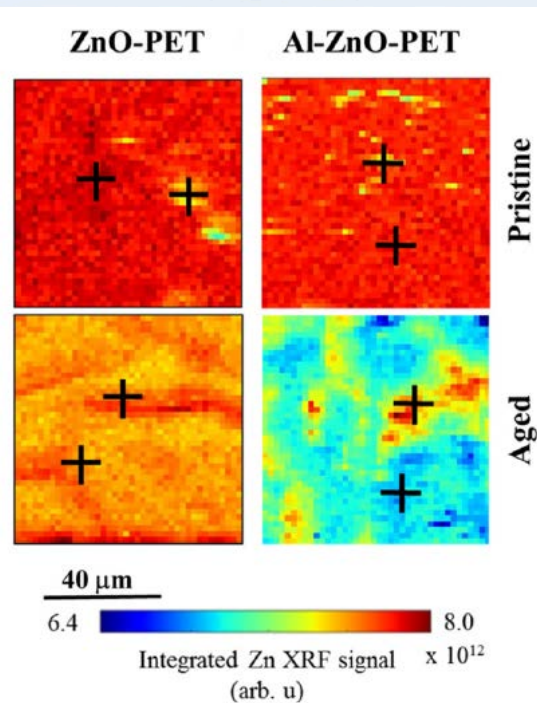


Key Future Development

- 1) Investigating **alternative additives** at SRX *in operando* to resolve dissolution issue: FeS_2 , TiS_2
- 2) Studying the key role of S by utilizing **future beamline capabilities with tender x-ray** spectroscopy
- 3) Applying **diffraction techniques at NSLS-II** to study structure and crystal-amorphous transition

In collaboration with Hong Gan and Ke Sun (Sustainable Energy Department, BNL), Chongang Zhao (Stony Brook U.)

Chemical and Structural Heterogeneity from Environmentally-Induced Aging of Zinc Oxide Films



X-ray fluorescence of the Zn distribution in non-doped ZnO and Al-doped ZnO on a PET substrate, pristine and aged under heat and humidity. Al-doped ZnO films showed the most significant degradation due to the formation of a Zn(OH)₂ phase where Al-doping contributes to defect-formation

H. Jiang, K. Chou, S. Petrash, G. Williams, J. Thieme, D. Nykypanchuk, L Li, A. Muto, and Y-c K Chen-Wiegart. *Applied Physics Letters* **109**: 091909 (2016).

Scientific Achievement

Showed nanoscale heterogeneity that compromises functions in ZnO thin films, particularly dominant in aluminum doped film after aging.

Significance and Impact

Understanding the degradation mechanism in ZnO thin films is important for a wide range of industrial applications, particularly in modern electronics.

Research Details

- Partnering with Henkel Corporation, a comprehensive study of the morphological and chemical heterogeneity of doped and undoped ZnO thin film was performed during aging on both conventional silicon and a flexible, transparent substrate.
- Advanced x-ray and electron methods were utilized synergistically at NSLS-II beamline 5-ID (SRX) and the Center for Functional Nanomaterials to provide a detailed understanding with multiple physical contrast mechanisms – imaging, spectroscopy and diffraction – and at wide range of spatial resolutions from atomic to sub-micron.

Work was performed at Brookhaven National Laboratory, Lawrence Berkeley National Laboratory, Henkel Corporation and Hitachi High Technologies America

XRF maps of U – loaded cotton swipe



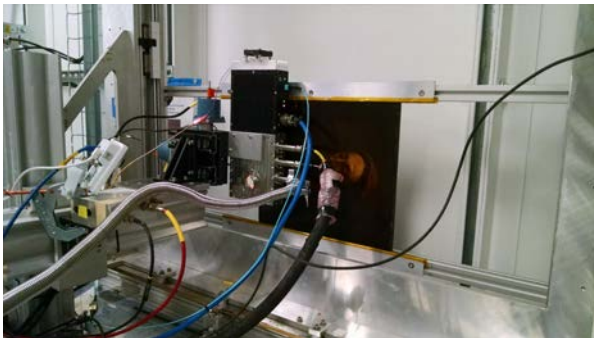
Test samples from International Atomic Energy Agency IAEA

Transformative capability of Maia: Fast large area scanning



10x10 cm swipe sample, loaded with NIST # 2584, plus added U particles.

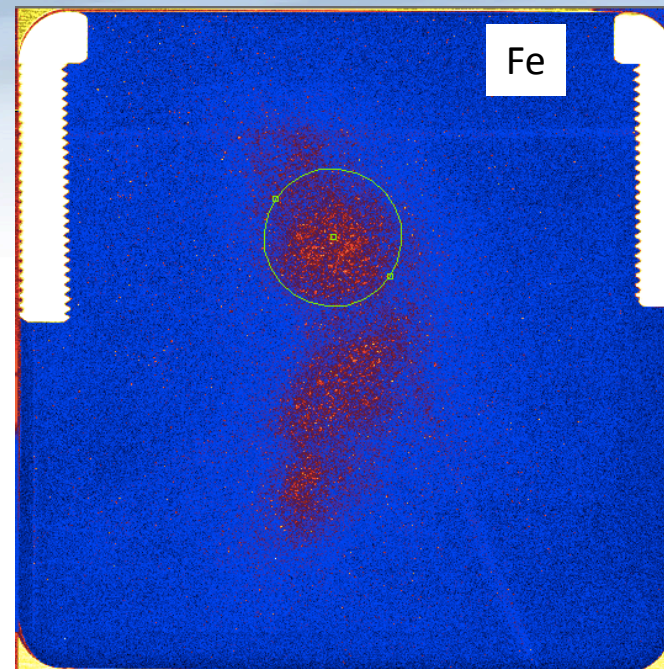
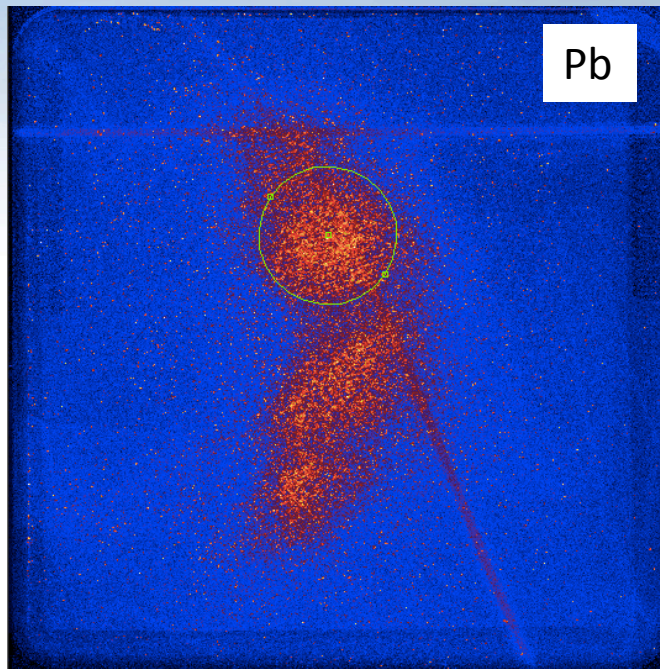
Sealed in plastic bag, held in place by frame. Seal stays untouched.



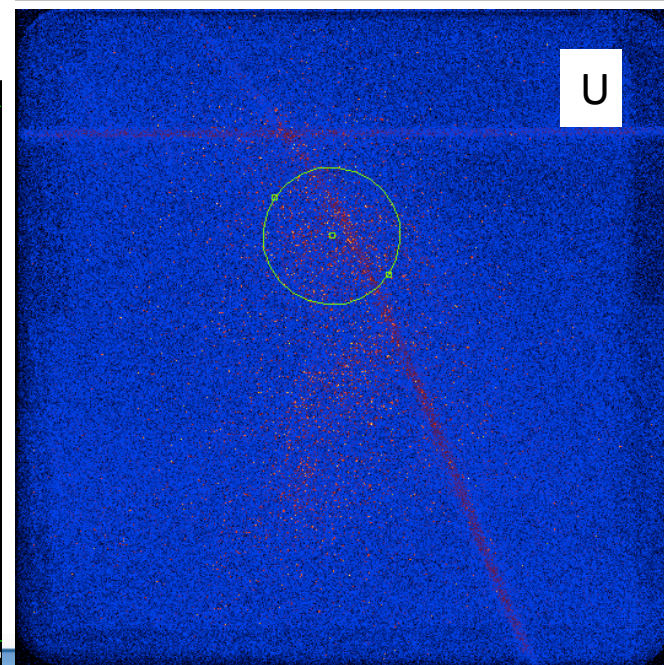
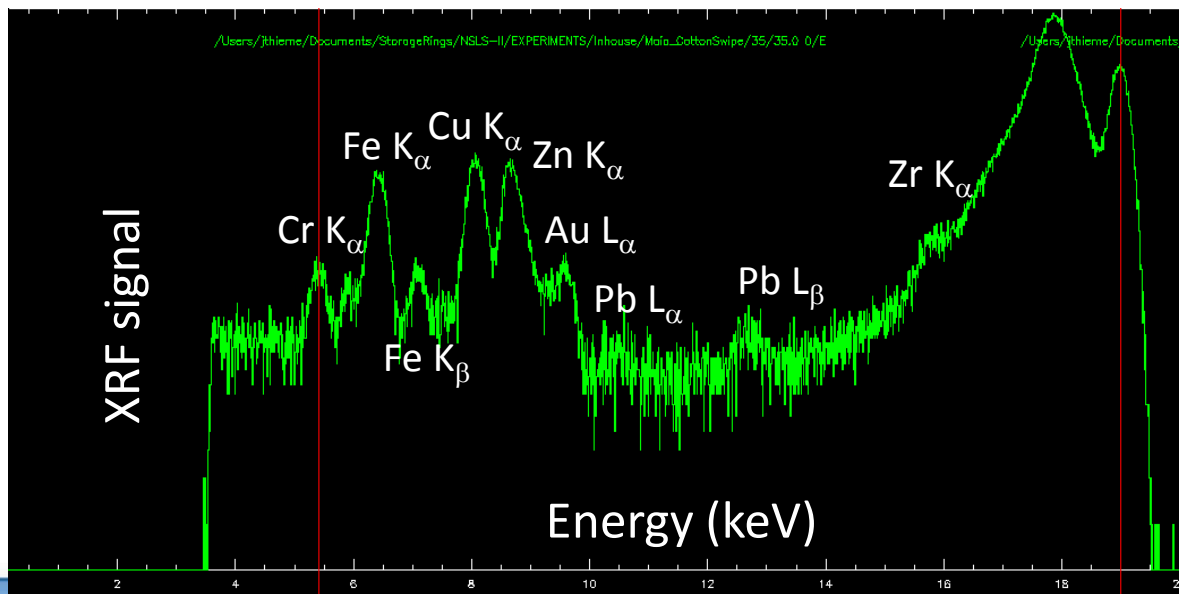
Standard Reference Material 2584:
Trace Elements in Indoor Dust
(Nominal mass fraction of 1 % Lead)
MSDS: “SRM 2584 is composed of dust collected from vacuum cleaner bags used in the cleaning of interior dwelling spaces.”

XRF maps of swipes

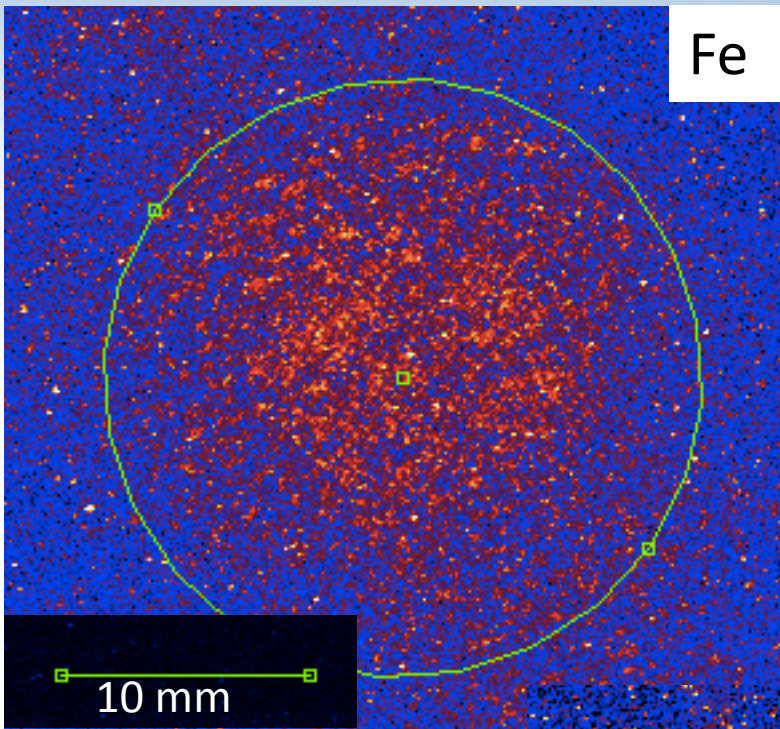
- 10x10 cm swipe
- elemental maps
- 100 μm pixel size
- 3hr collection time



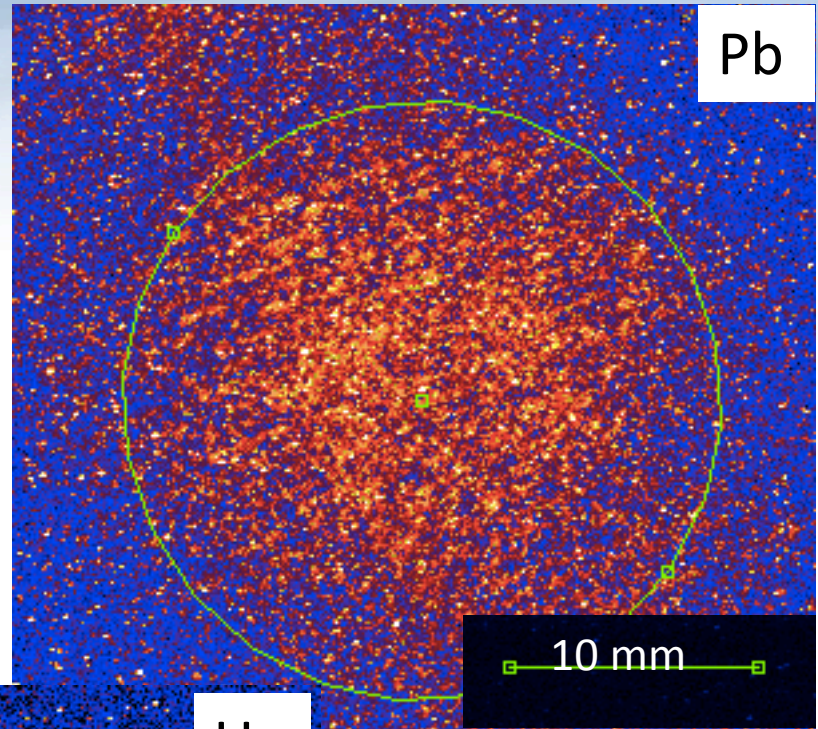
XRF spectrum at one pixel of swipe



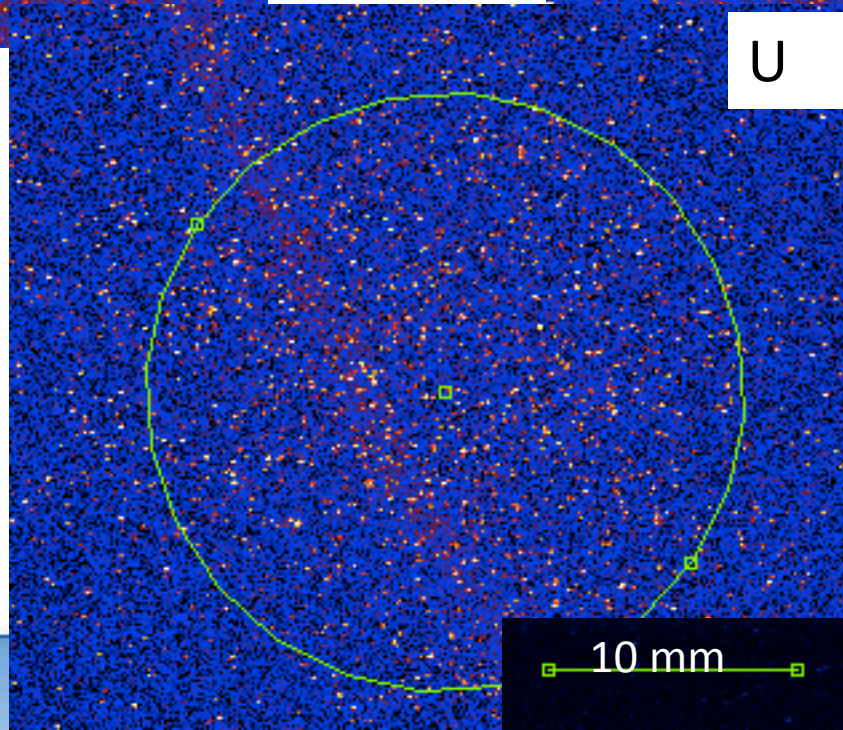
Fe



Pb



U



XRF maps of swipes

Fe-Pb strongly correlated.
U dispersed.

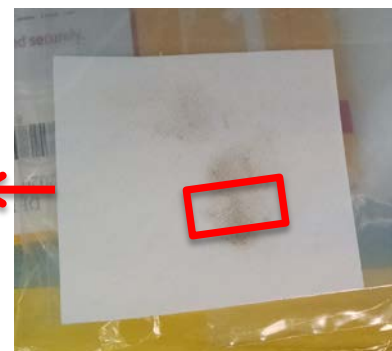
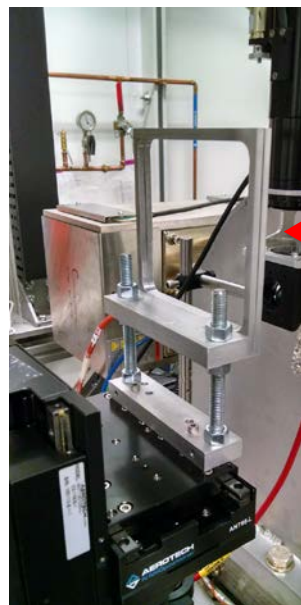
XRF maps of U – loaded cotton swipe



Test samples from International Atomic Energy Agency IAEA

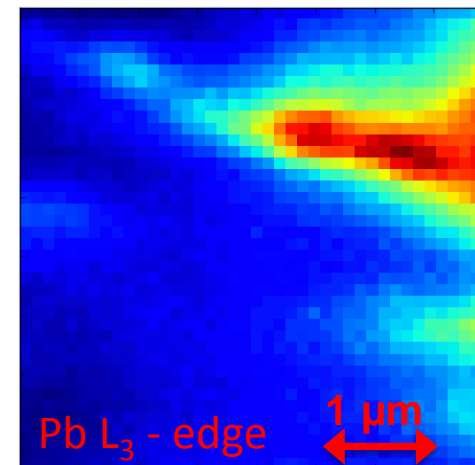
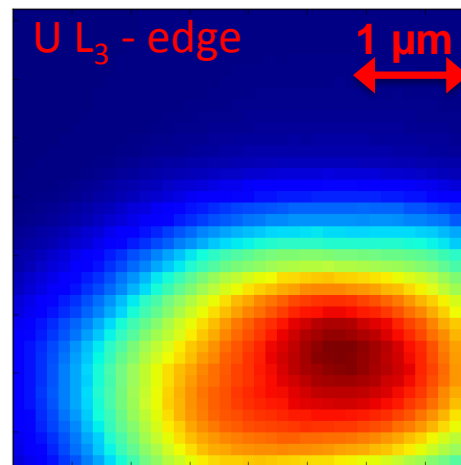
Scan across
cotton swipe.
Mapping at
Uranium
 L_3 - edge

$700 \times 200 \mu\text{m}^2$
 $5 \mu\text{m}$ step size



$10 \times 10 \text{ cm}^2$ cotton swipe mounted
in sample frame with PE bag,
thus without interfering with
sample integrity.

Zooming in

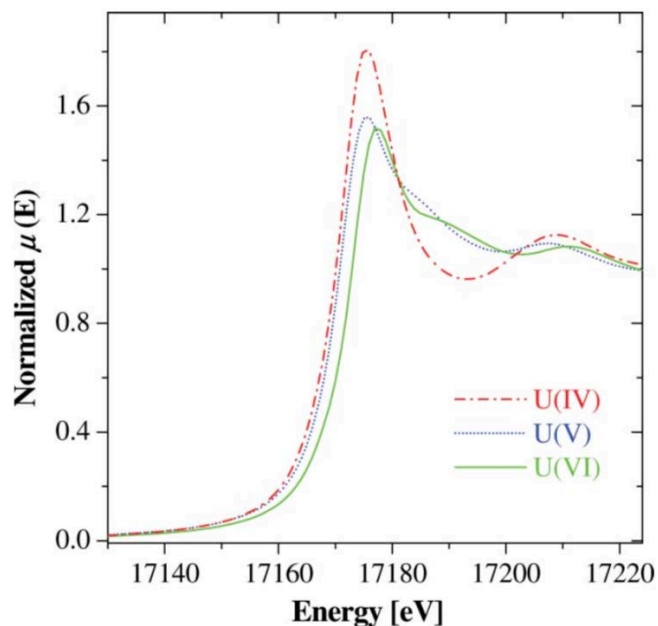


$16 \times 16 \mu\text{m}^2$, $0.4 \mu\text{m}$ step size

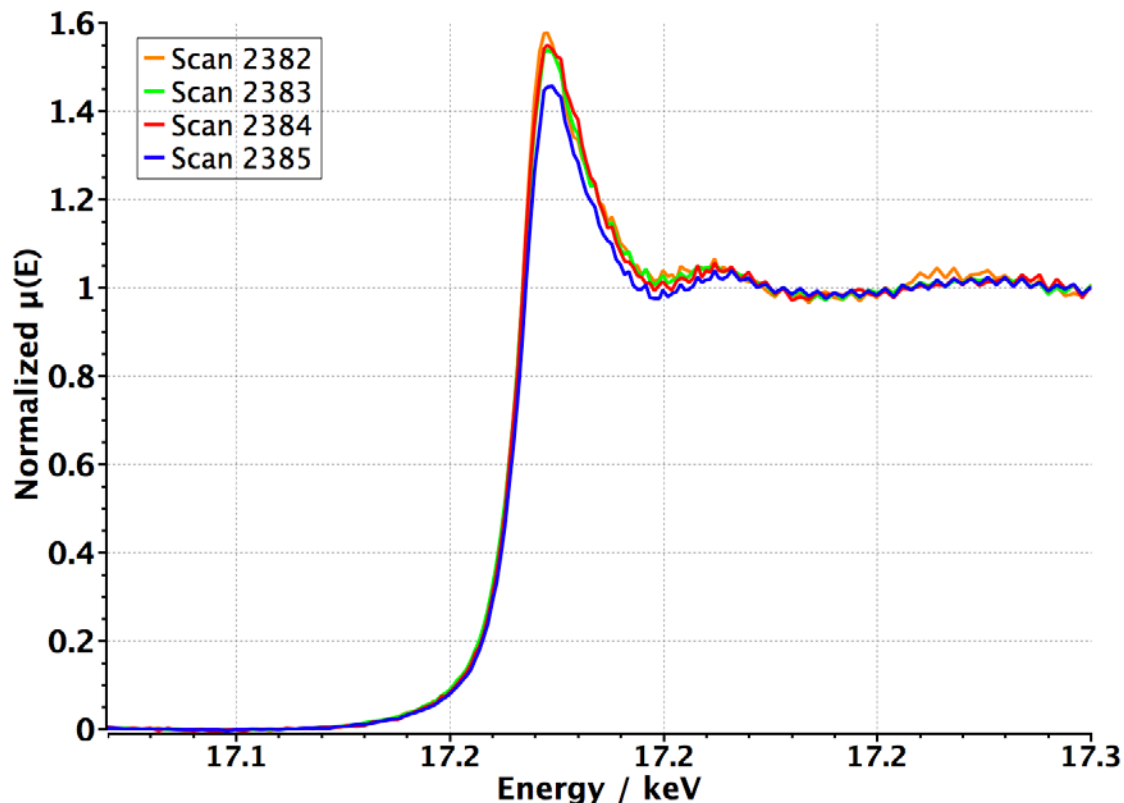
U L₃ – edge XANES spectroscopy

Results show **Uranium Oxide**, as can be found in **yellowcake**, predominantly in the sample.

Comparison with Literature



C. Henning et al., *Dalton Trans.*, 2010, **39**, 3744–3750

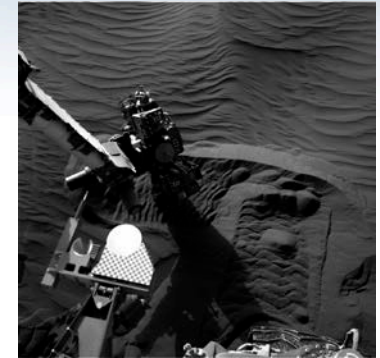


U L₃ - edge XANES from four different uranium hot spots

Sample Return Mission from Mars

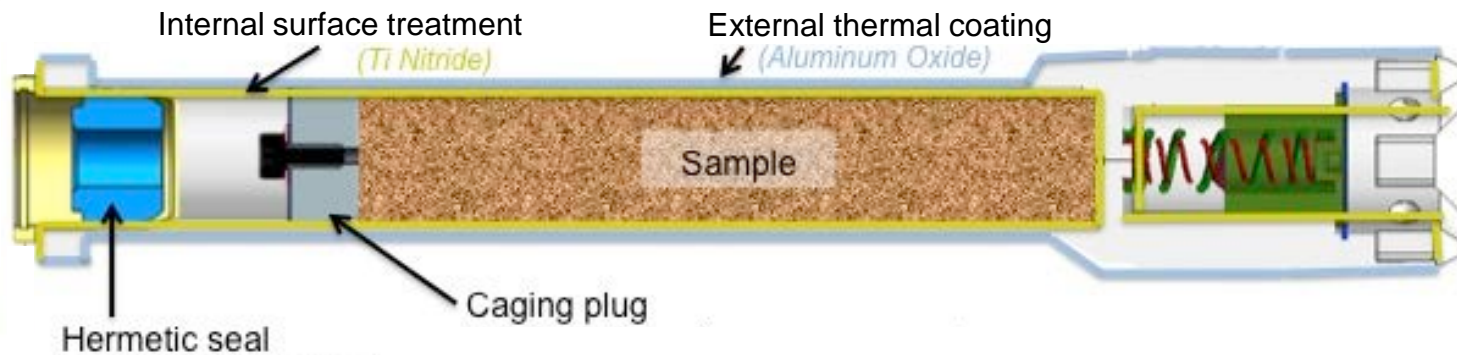
3 missions discussed / planned

1. Rover evaluating and collecting samples (~ 30)
2. Rover retrieving samples, lifting them into orbit
3. Satellite shipping samples back to earth

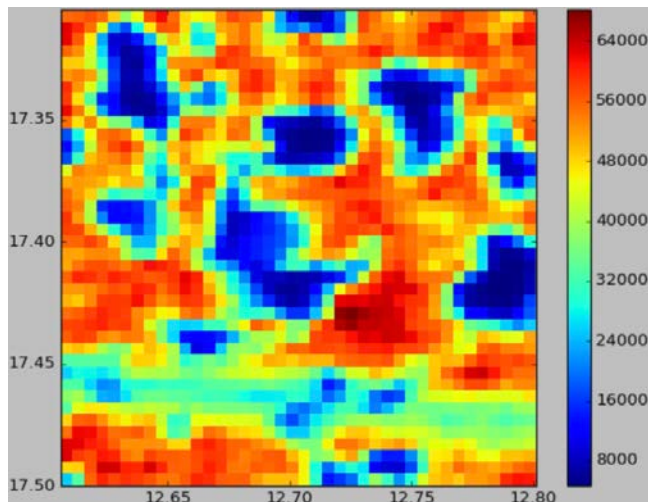


Problem: How to study samples within the tube without opening it?
External building to treat samples and avoid contamination

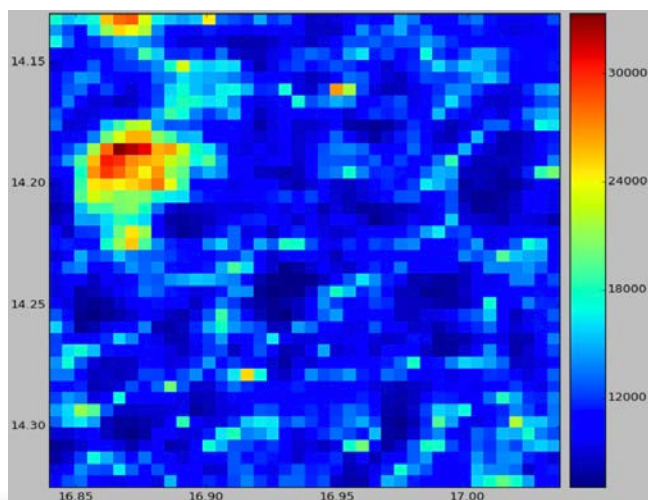
Possible solution: Synchrotron Radiation



Fitting X-ray fluorescence from banded iron formation to show Fe distribution

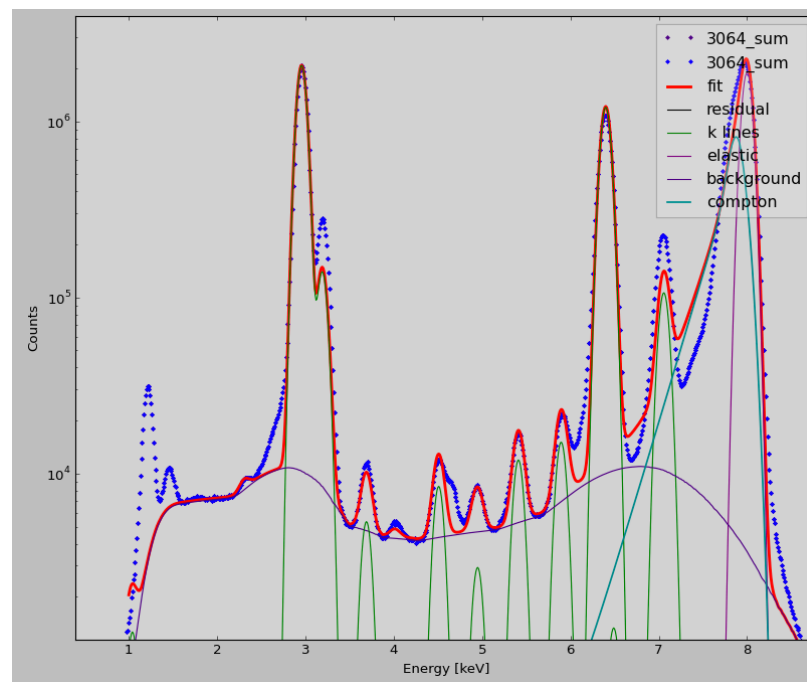


Fe-rich area,
direct acquisition



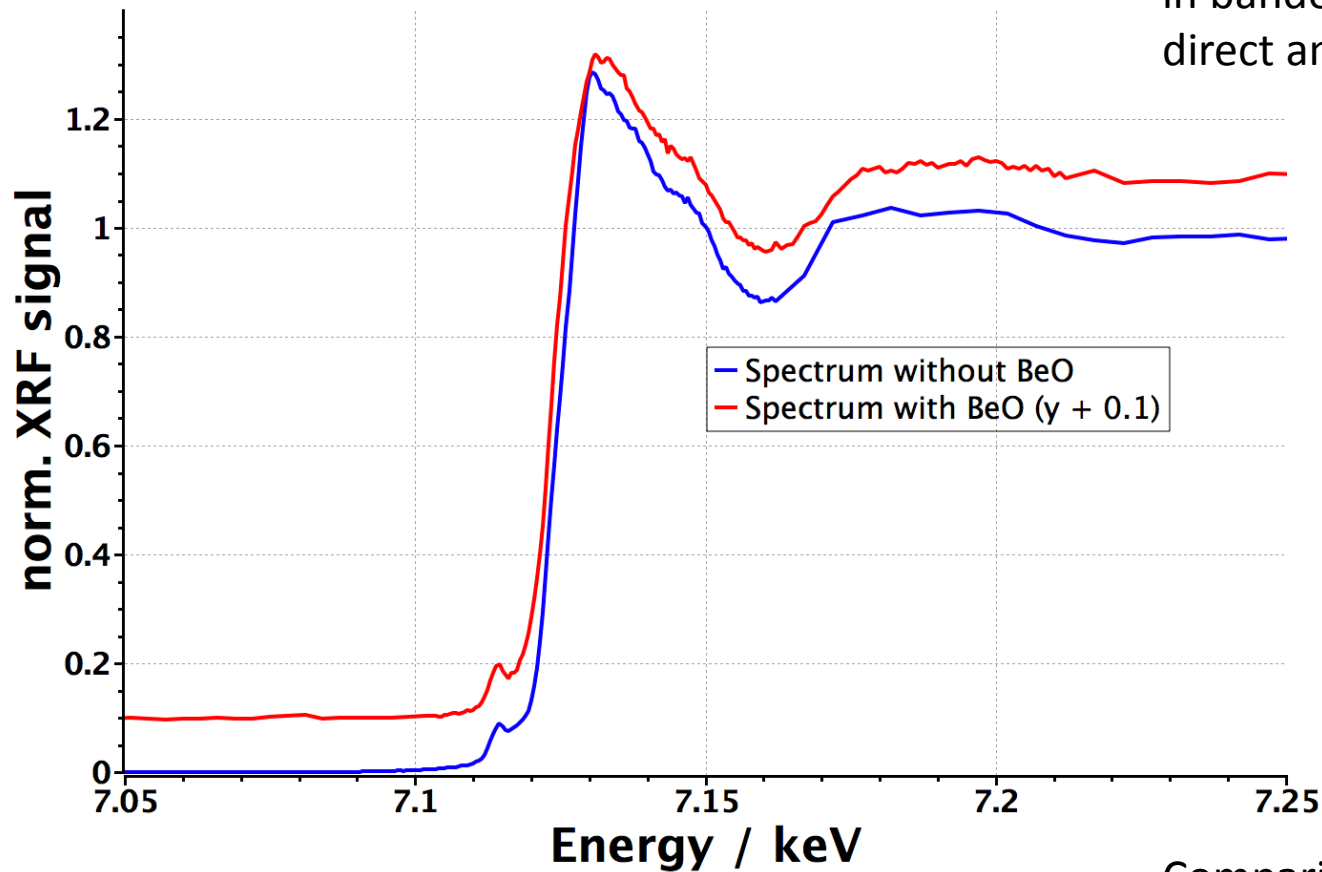
XRF measured through
500 μm BeO, area with
less dominant Fe signal

X-ray fluorescence spectrum,
measured through 500 μm BeO,
showing Fe and other elements.



Software: PyXRF

XANES spectra at Fe K-edge of banded iron formation



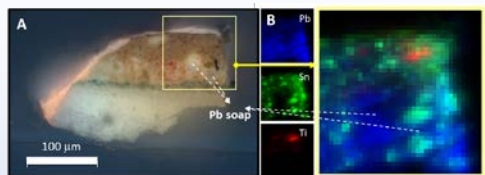
Two spectra from an Fe-rich area in banded iron formation sample, direct and through 500 μm BeO

Spectra have been fitted and normalized using Athena software.

Y-axis of spectrum obtained through BeO elevated for better comparability.

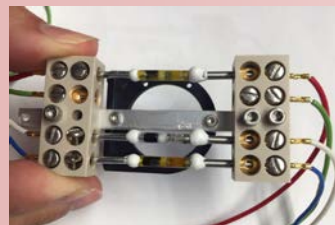
Comparison shows there is no influence of BeO on spectra.

Art Conservation

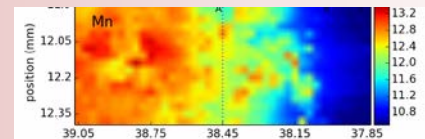


Pb-soap Formation

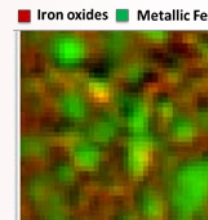
Novel Energy Storage Systems:



Li-S Battery

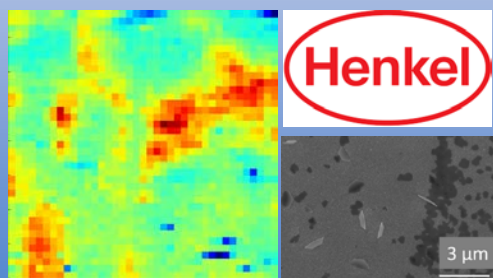


Aqueous
Low-cost battery



CNT additives

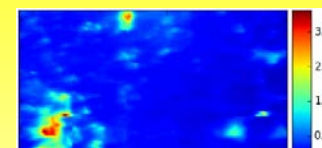
Industrial Application



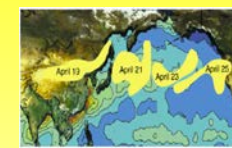
Heterogeneity
In ZnO thin film

Thank you!

Environment Science

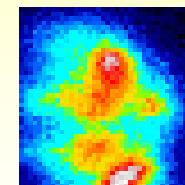


Soil Science



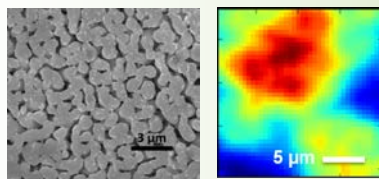
Aerosols

Biology



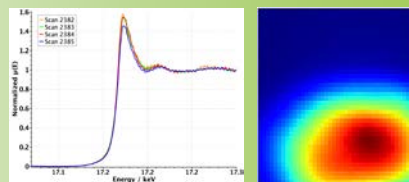
Subcellular
element distribution

Materials Science



Nano-porous Materials

Nuclear Forensics



Uranium Chemical Analysis