united nations educational, scientific and cultural organization
international atomic energy agency

the **abdus salam** international centre for theoretical physics

ICTP 40th Anniversary

SCHOOL ON SYNCHROTRON RADIATION AND APPLICATIONS
In memory of J.C. Fuggle & L. Fonda

19 April - 21 May 2004

Miramare - Trieste, Italy

1561/37

Scanning X-ray microscopy

J. Kirz

Scanning X-ray microscopy
and diffraction imaging

Janos Kirz
Stony Brook University

Outline

- 1/ History – as I see it
  - Comments on X-ray microprobes
- 2/ STXM at the NSLS and elsewhere
- 3/ Variations: SPEM, SLXM, SXRF
- 4/ Diffraction based imaging
- 5/ Conclusions
  - where different forms of x-ray microscopy fit in.

H. H. Pattee Jr.
The Scanning X-ray Microscope
JOSA 43, 61 (1953)

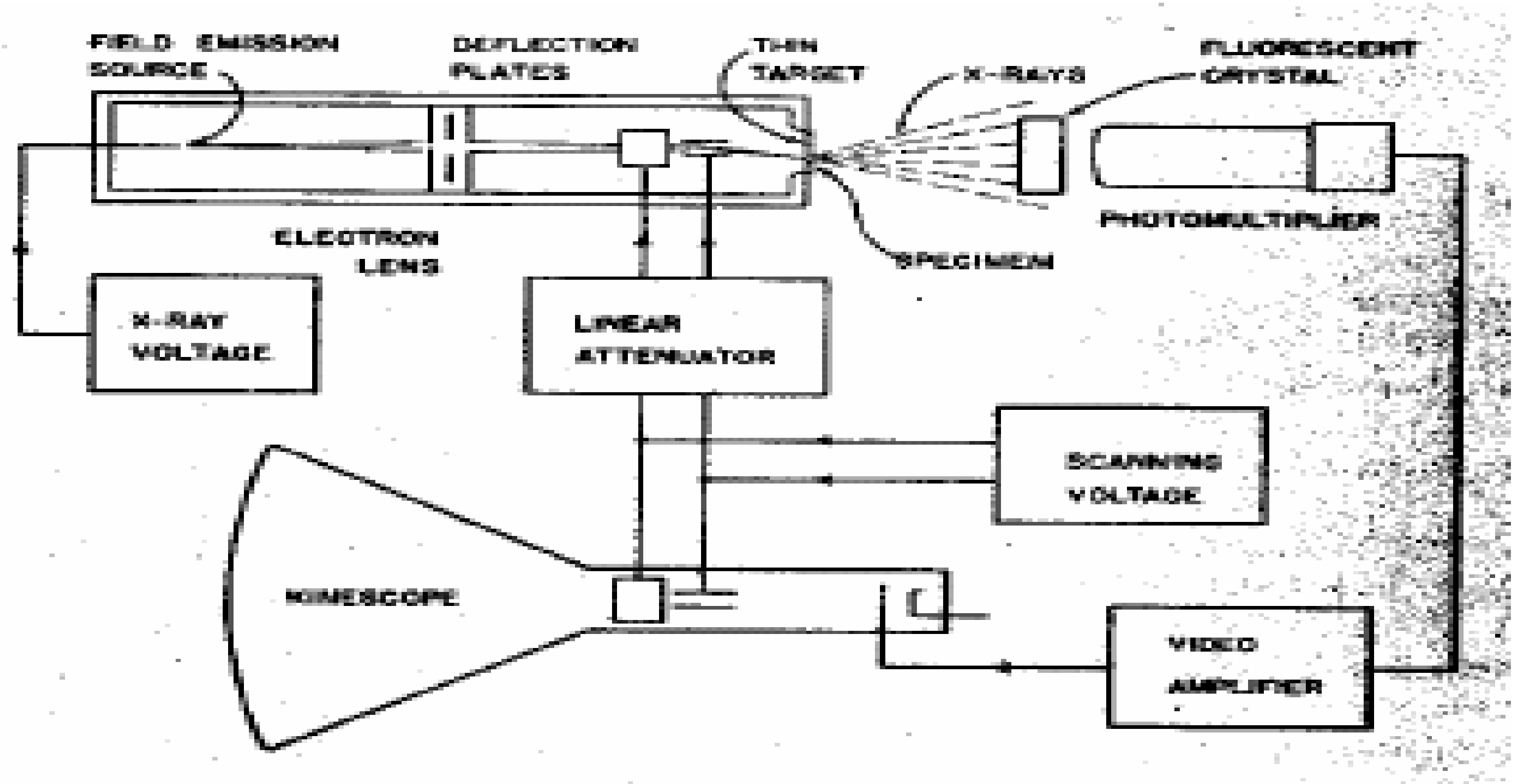
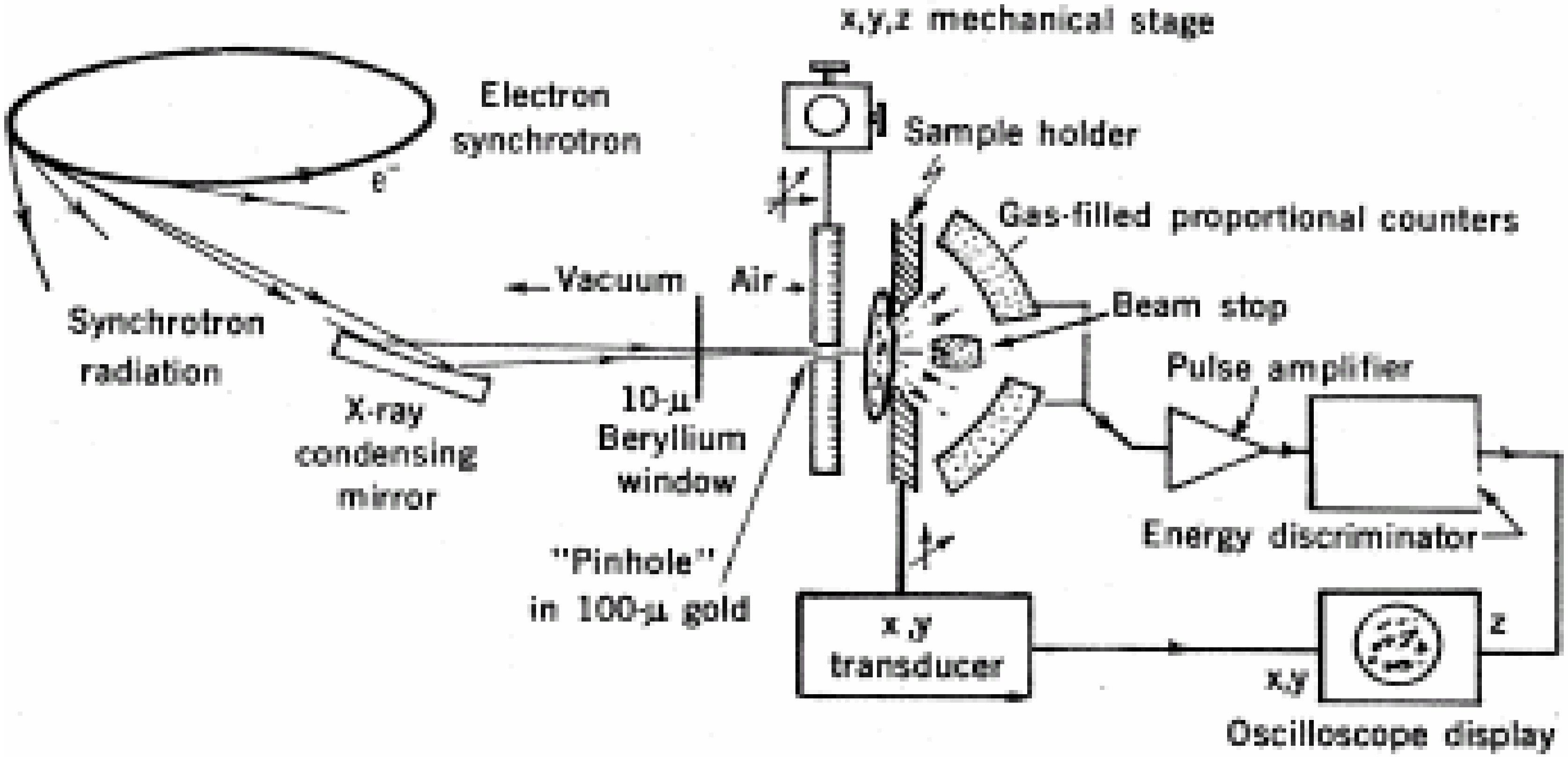


FIG. 1. Scanning x-ray microscope.

Horowitz and Howell
A Scanning X-ray Microscope using Synchrotron Radiation
Science, 178, 608 (1972)



Horowitz and Howell
1-2 micron pinhole collimator

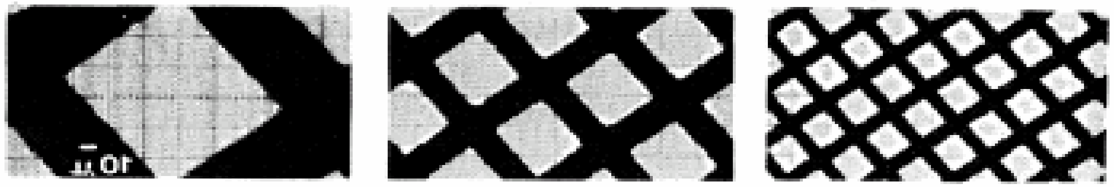


Fig. 2. Transmission micrographs of a 200 mesh per inch (80 grids per centimeter) copper grid at three different magnifications. The faint horizontal and vertical lines in these micrographs are from the oscilloscope graticule.

transmission

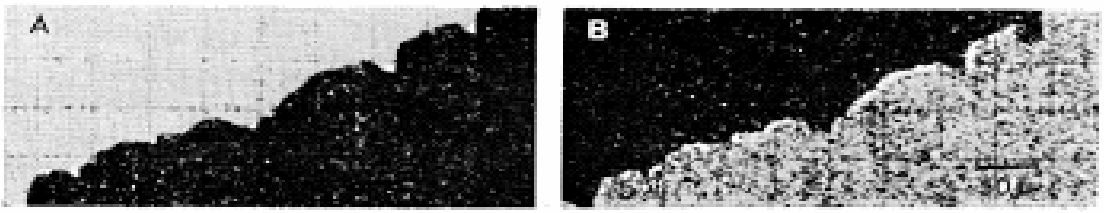


Fig. 3. An aluminum foil 10 µ thick viewed: (A) in transmission and (B) in aluminum K fluorescence.

transmission and Al fluorescence

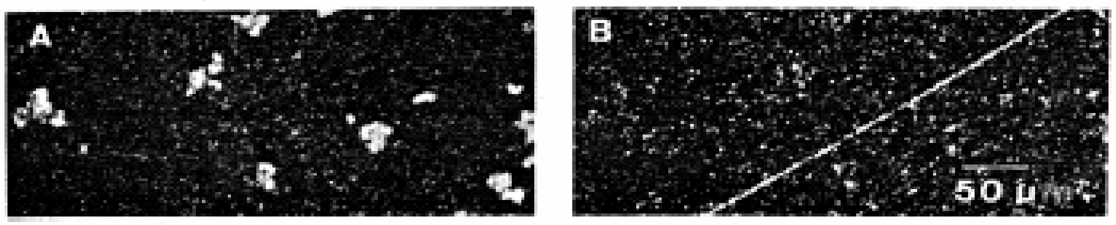


Fig. 4. A sample consisting of sulfur dust and a 2-µ silicon whisker viewed: (A) in sulfur K fluorescence and (B) in silicon K fluorescence.

S and Si fluorescence

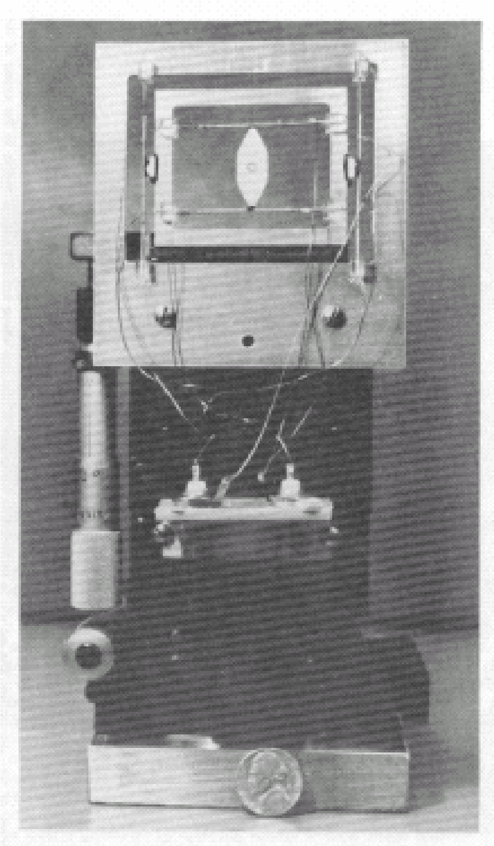
Scanning microscopy

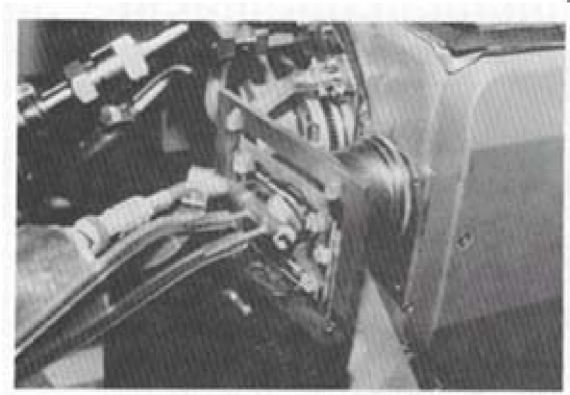
- Scan specimen (or probe) mechanically
  - Collect image pixel by pixel
- Detect
  - transmitted x-rays (STXM),
  - fluorescence (SXRF)
  - photoelectrons (SPEM)
  - visible light (SLXM)
  - diffracted X-rays
- Size of microprobe determines resolution
  - here ~ 2 μ, formed by pinhole
- Brightness limited
- Scan parameters determine object area, “magnification”

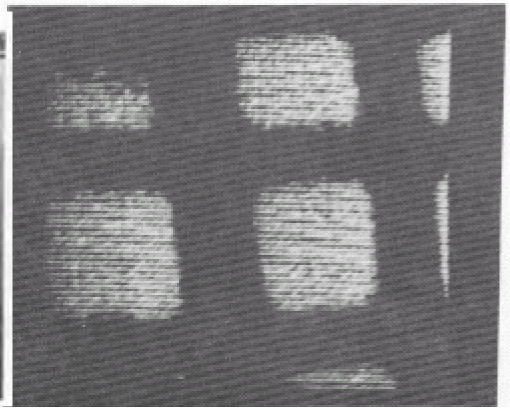
1979
Plans for a scanning transmission X-ray microscope

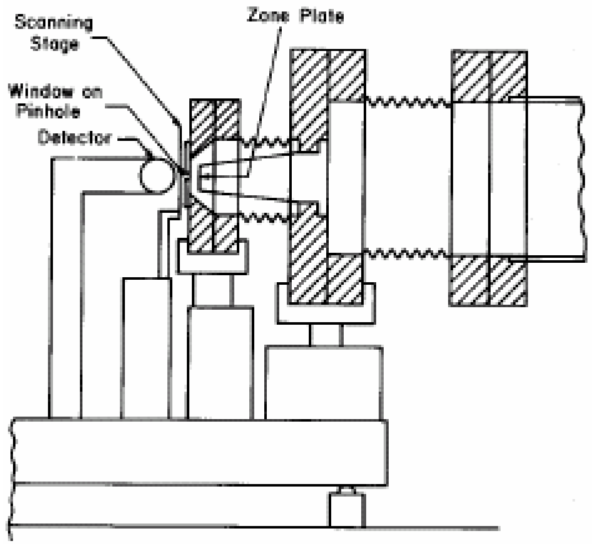
J. Kirz, R. Burg and H. Rarback

Ann. NY Acad. Sci. 342, 135 (1980)

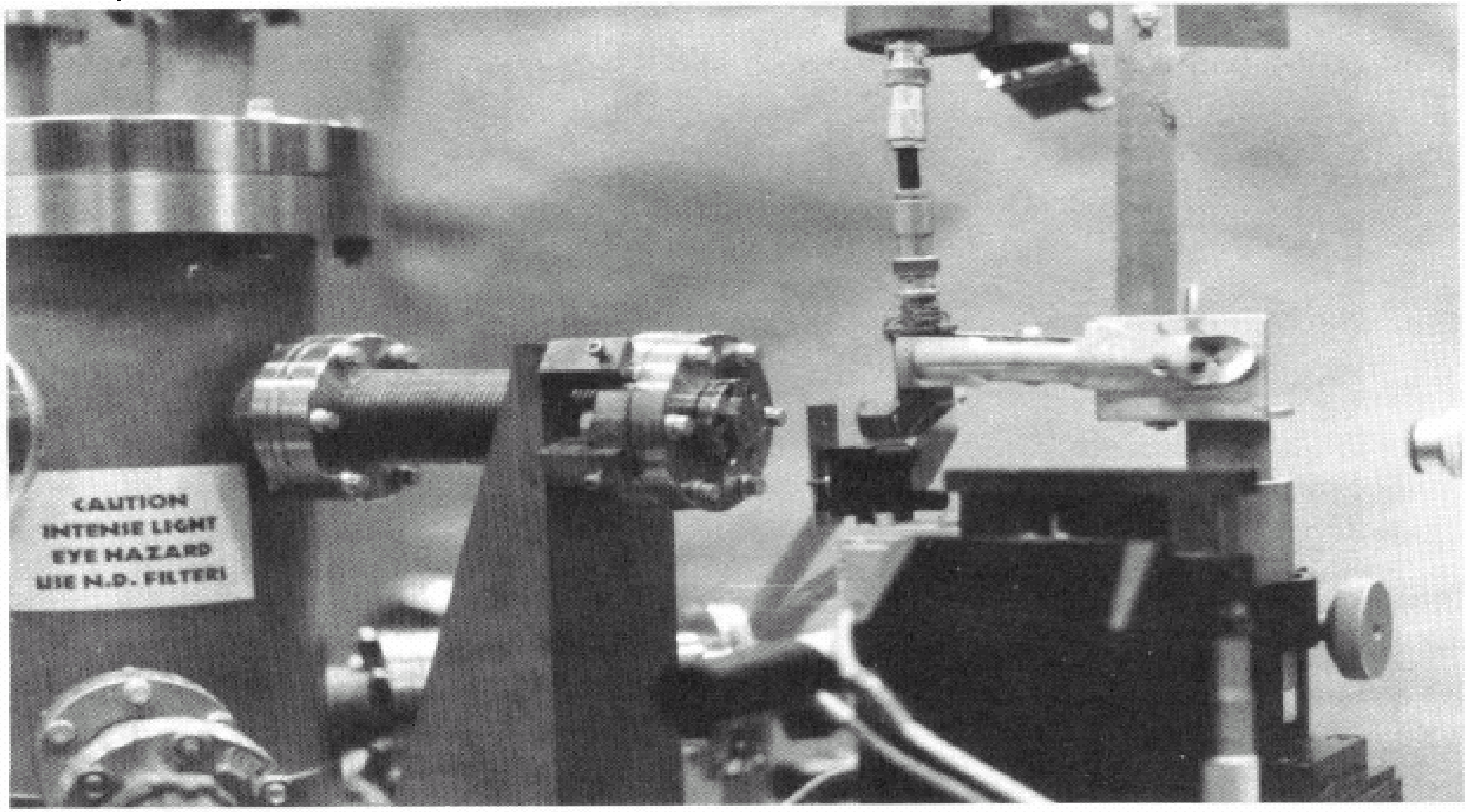




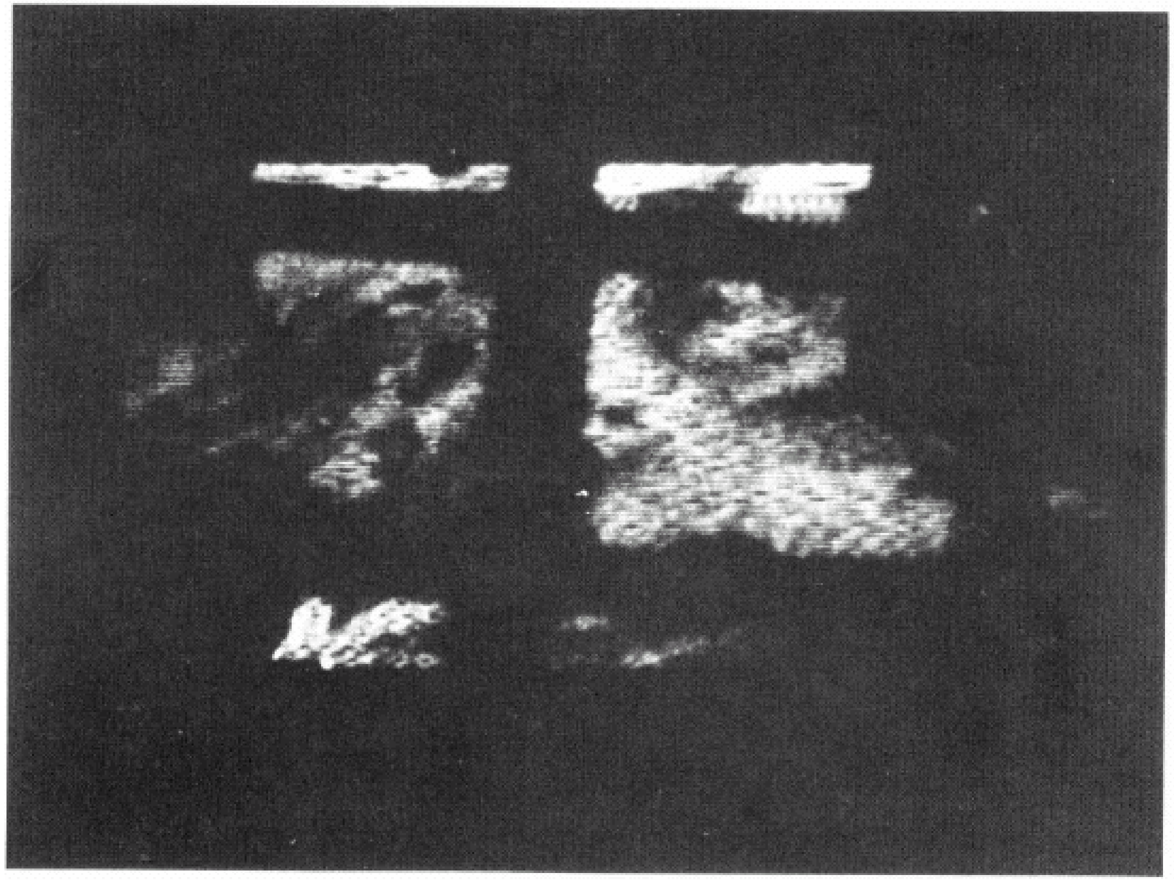




H. Rarback et al.
Scanning soft X-ray microscopy – first tests with synchrotron radiation. (SSRL)
(Scanned Image Microscopy, E. A. Ash ed. 1980 (449 – 455)

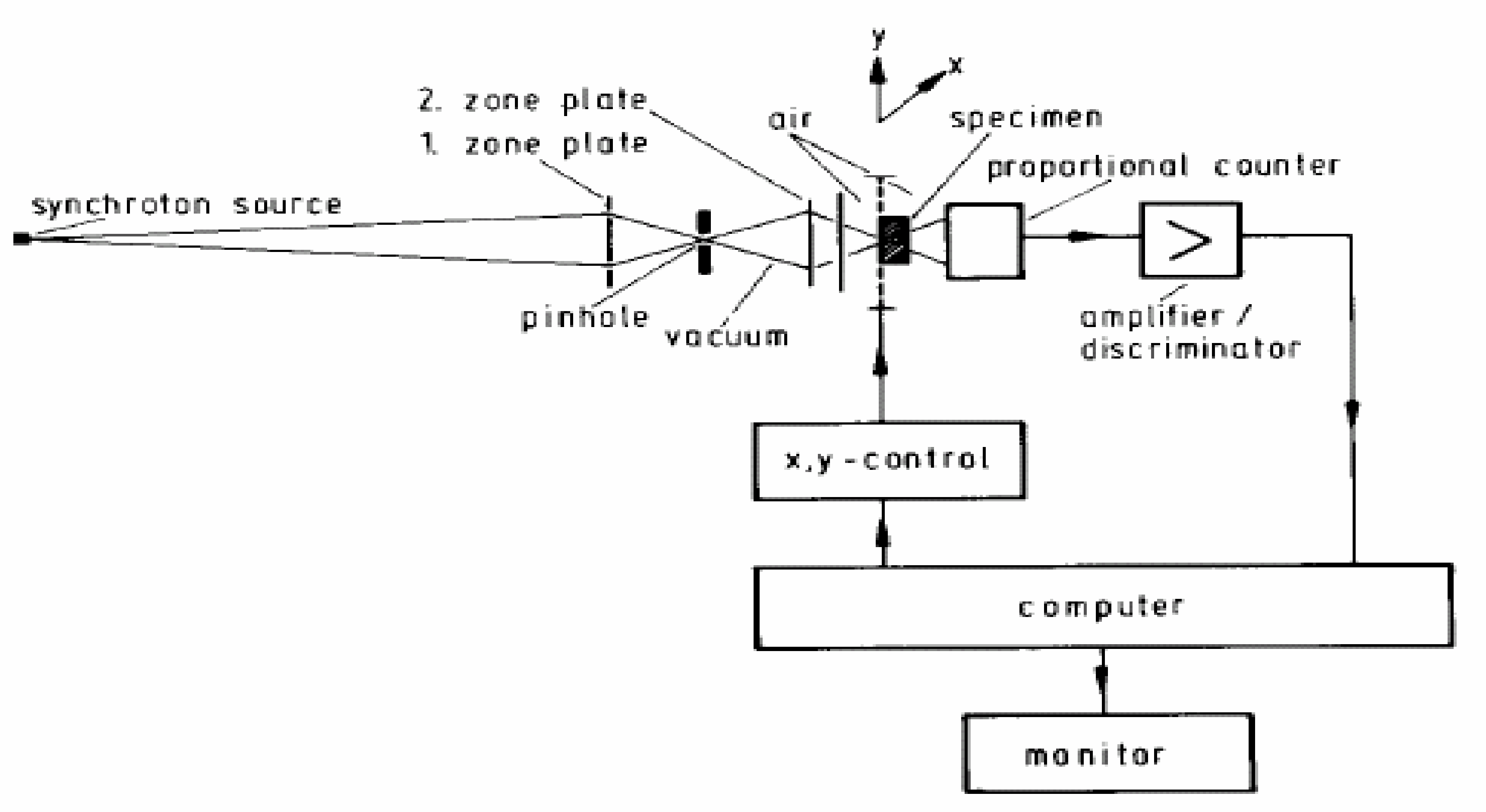


Micrograph of a wet muscle-cell culture
image area: 350 x 500 microns
1 micron pinhole forms probe; 200-280 eV

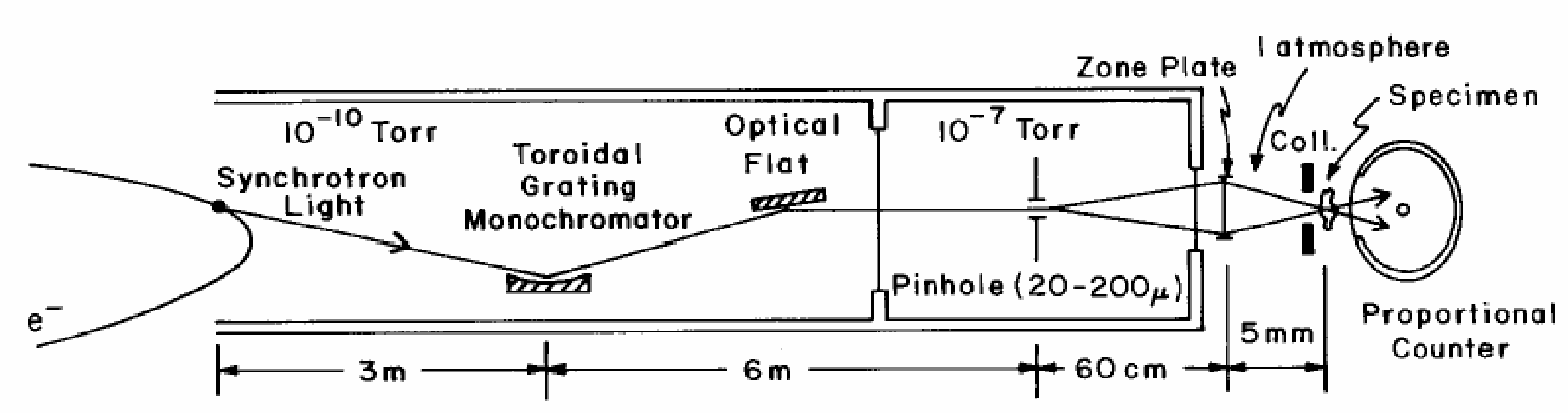


Specimen courtesy of J. Narbonne & J. Pine

Imaging and scanning soft X-ray microscopy with zone plates
G. Schmahl, D. Rudolph, B. Niemann
Scanned Image Microscopy, E. A. Ash ed. 1980 (393 – 412)



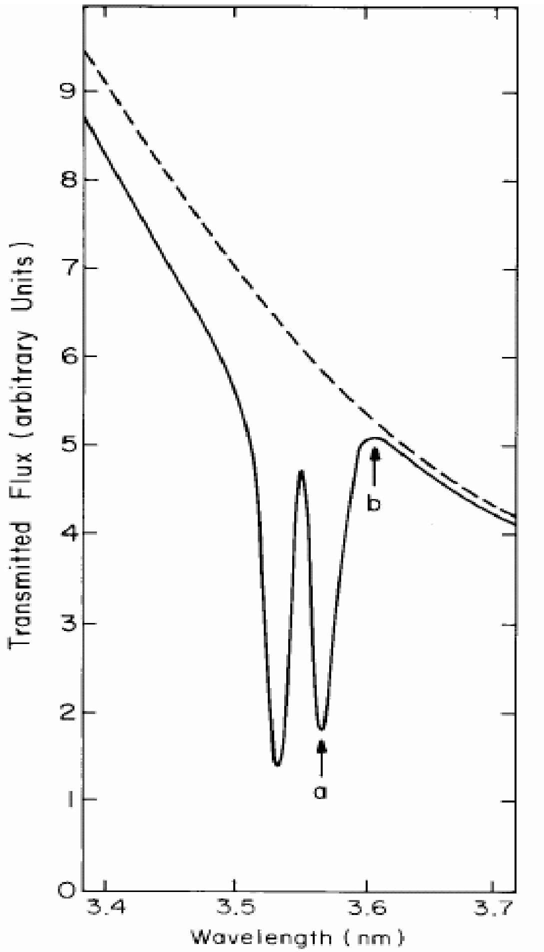
Scanning microscopy (STXM) 1983

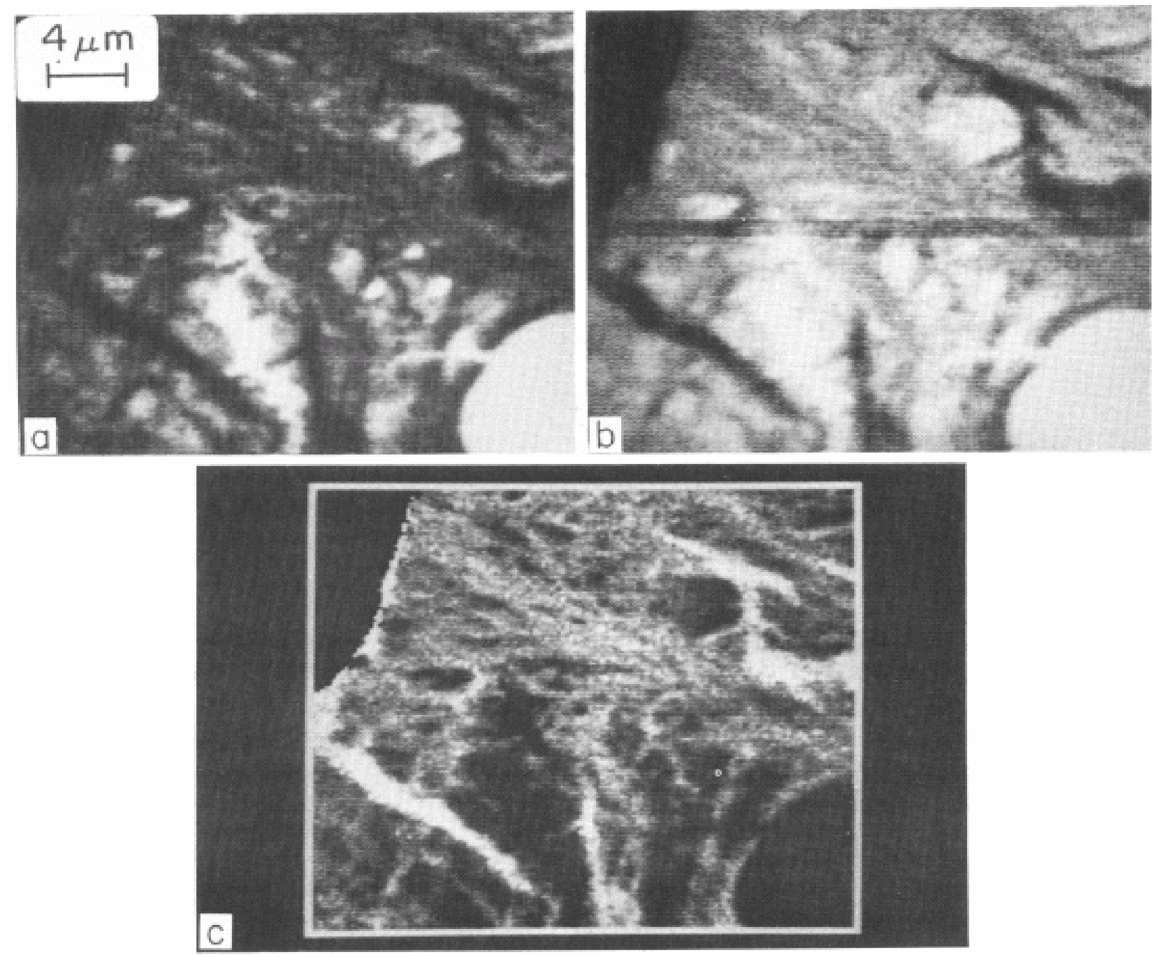


- Silicon nitride window
- Zone plate
- Proportion counter
- Scanning stage

Kenney J. Microsc.1984

Absorption microanalysis with a scanning X-ray microscope: mapping the distribution of calcium in bone
J. Kenney et al, J. Microsc. 138, 321 (1985)



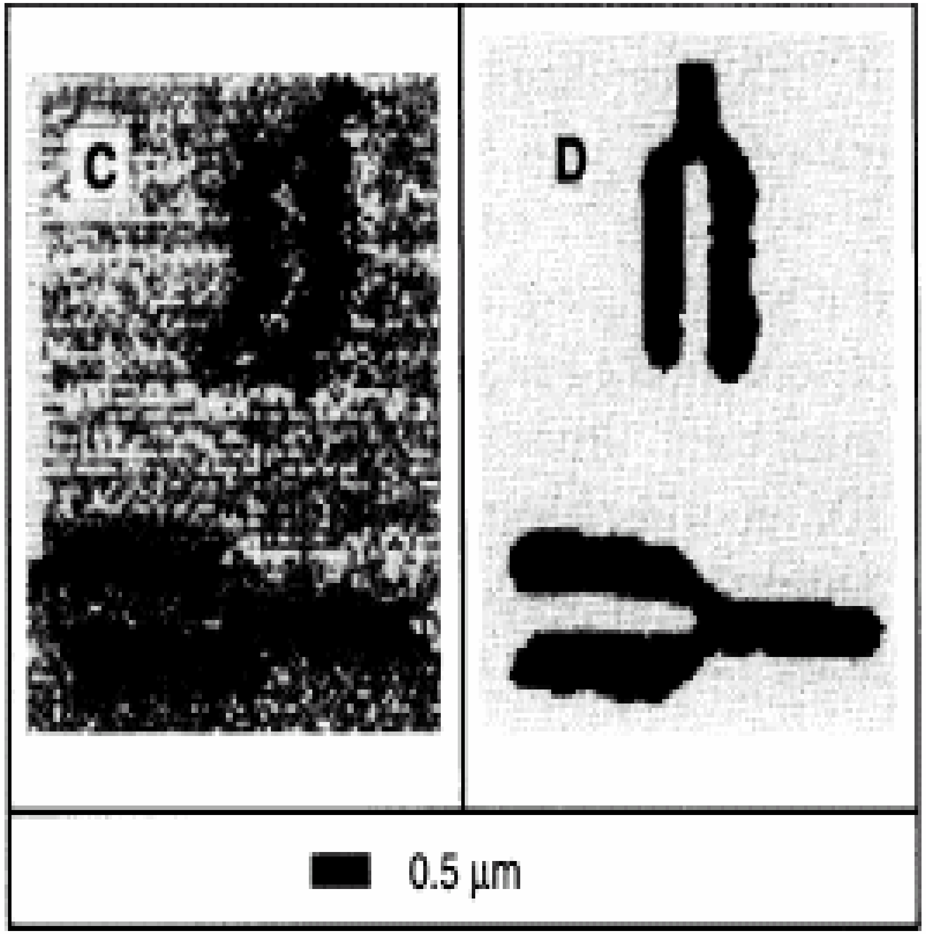


Comments on the formation of the probe

- Major types:
  - Pinholes; Tapered capillaries; Waveguides
    - Mostly for high energy X-rays
  - Mirrors
    - Normal incidence (multilayer) - <200 eV
    - Grazing incidence 3 – 30 KeV
  - Lenses
    - Compound refractive – high energy
    - Zone plates 200 eV – 20 KeV

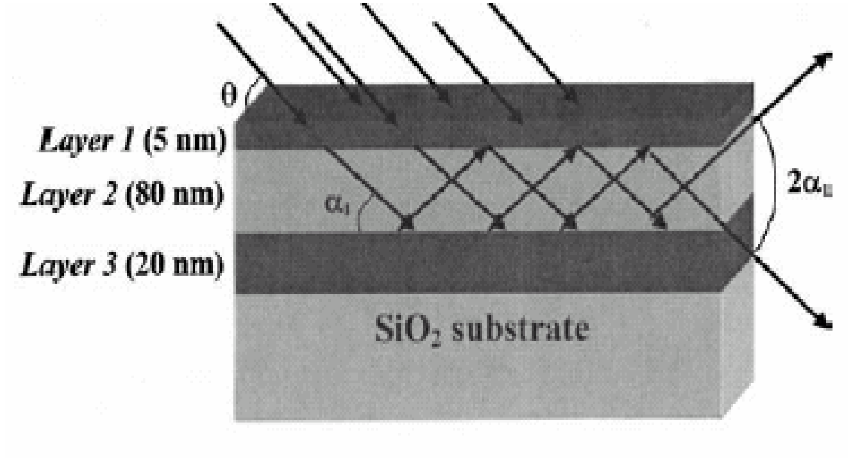
Tapered capillaries

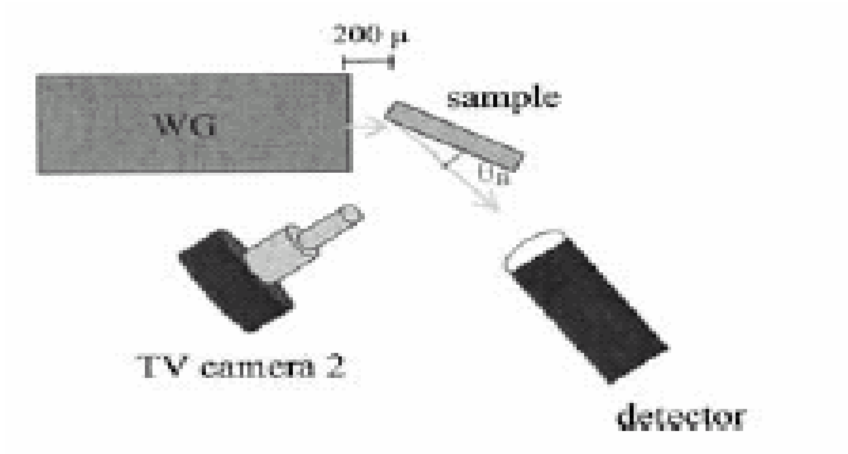
D. H. Bilderback, S. A. Hoffman, & D. J. Thiel, Science 263, 201 (1994)



Waveguides

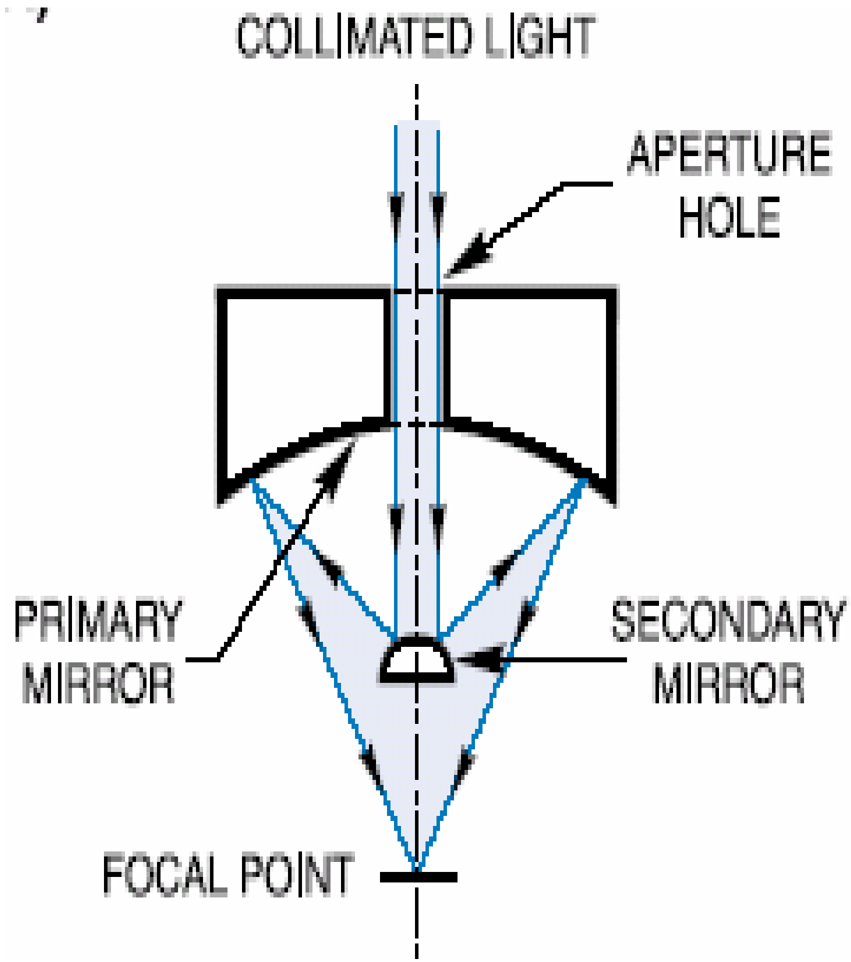
A. Cedola, S. Lagomarsino, F. Scarinci, M. Servidori, V. Stanic, J. Appl. Phys. 98, 1662 (2004)





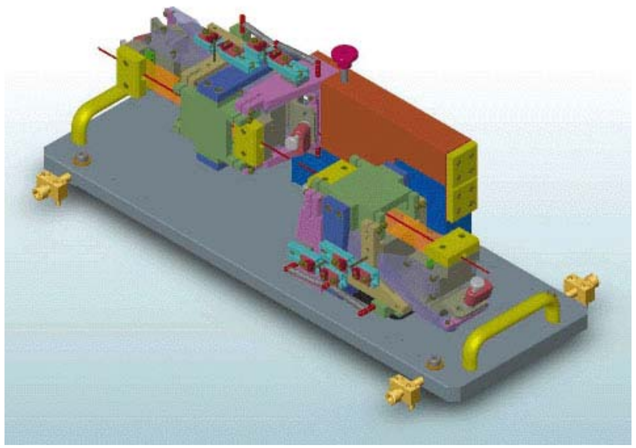
Mirrors – normal incidence

- Schwarzschild objective
- Multilayer coating:
  - Spiller
- First attempt: R.-P. Haelbich, W. Staehr, C. Kunz, HASYLAB 1980
- Hoover – NASA
- MAXIMUM
- SuperMAXIMUM



Mirrors – grazing incidence

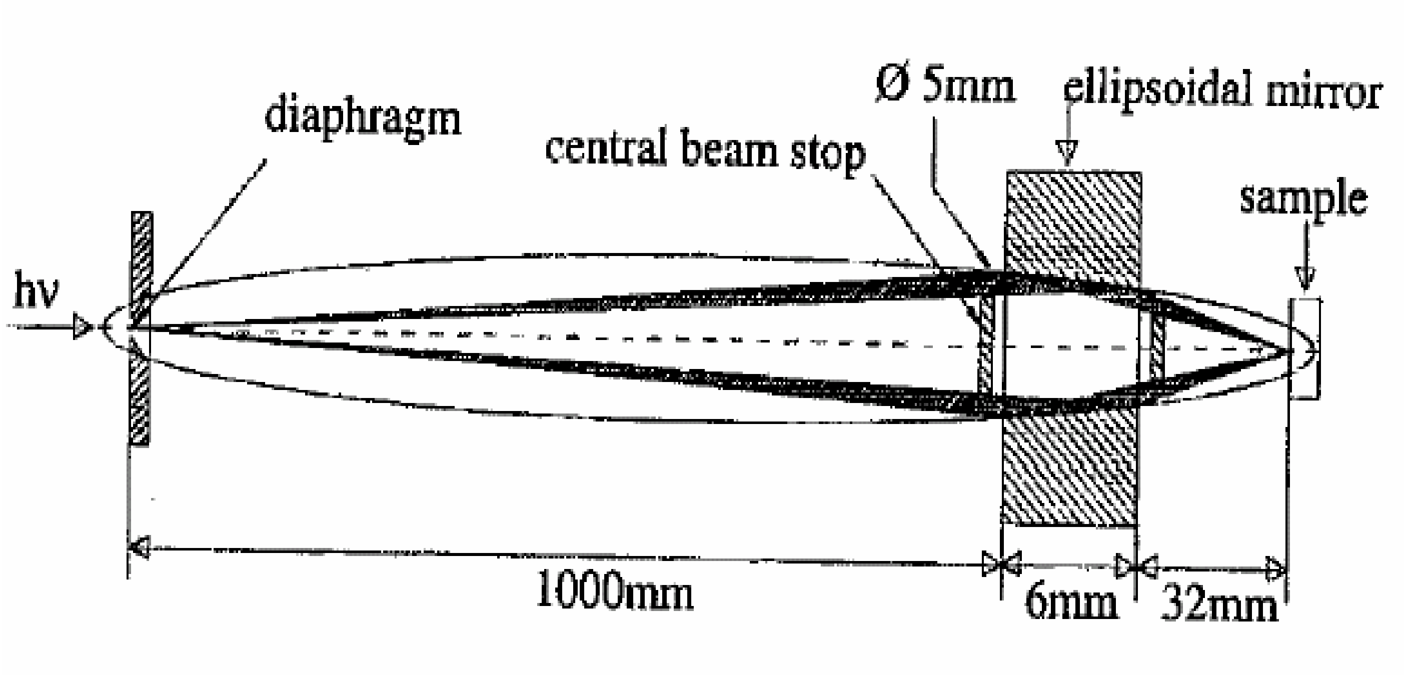
- achromatic!
- Kirkpatrick-Baez: separate x and y focusing
- Elliptical bending
- 100 nm focal spot (A. Freund et al. ESRF)



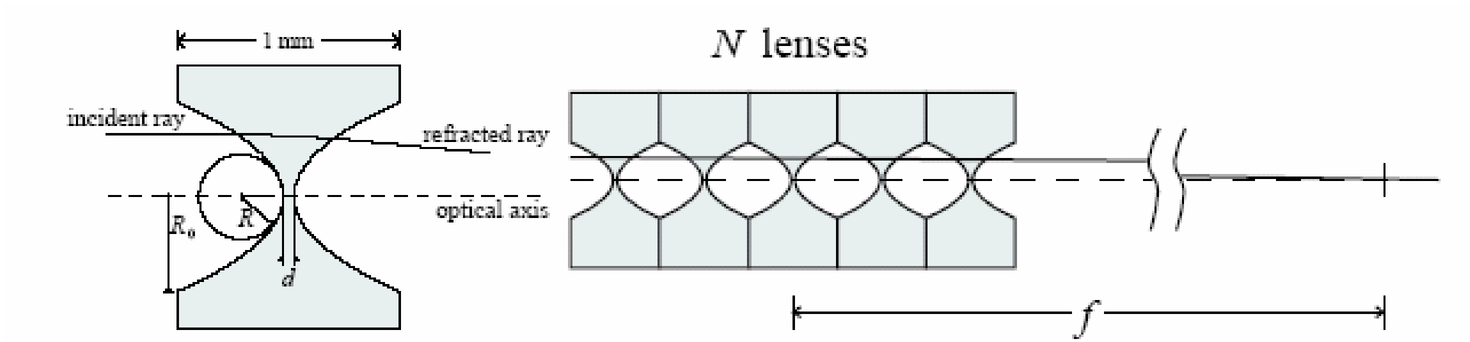
Mirrors – grazing incidence

- Ellipsoids:

  J. Voss, H. Dadras, C. Kunz, A. Moewes, G. Roy, H. Sievers, I. Storjohann, and H. Wongel, J. X-ray Sci. Technol. 3, 85 (1992).



Parabolic refractive lenses ESRF/Aachen collaboration



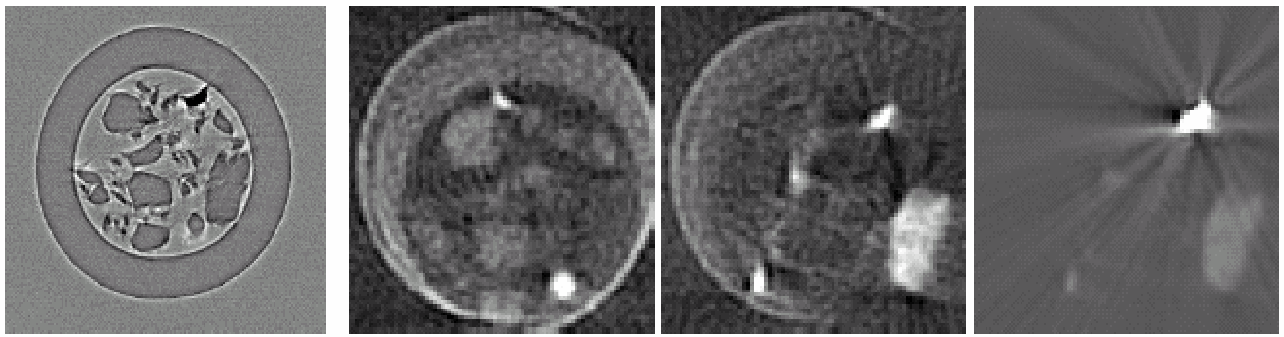
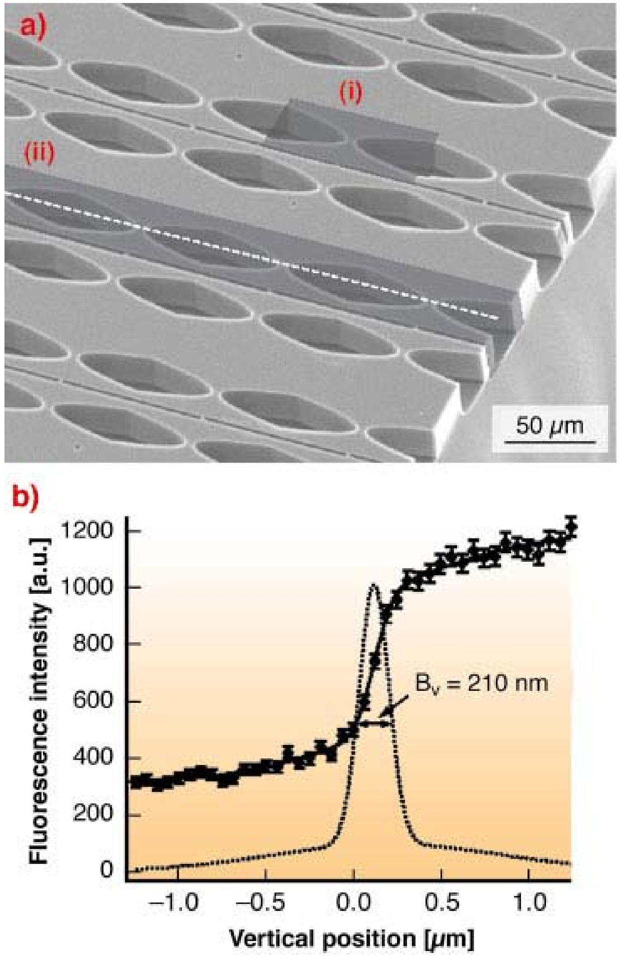


Figure 2: Results a combined transmission and fluorescence microtomography study. The sample consisted of different particles in a glass capillary (inner diameter 100 μm. The capillary wall as well as the particle outlines are clearly visible in the transmission tomogram of a slice in the sample (*far left*). The three images on the right are fluorescence tomograms of the same slice for different energies of the fluorescence radiation, namely Zr-K_α (*left center*), K-K_α (*right center*), and Fe-K_α (*far right*).

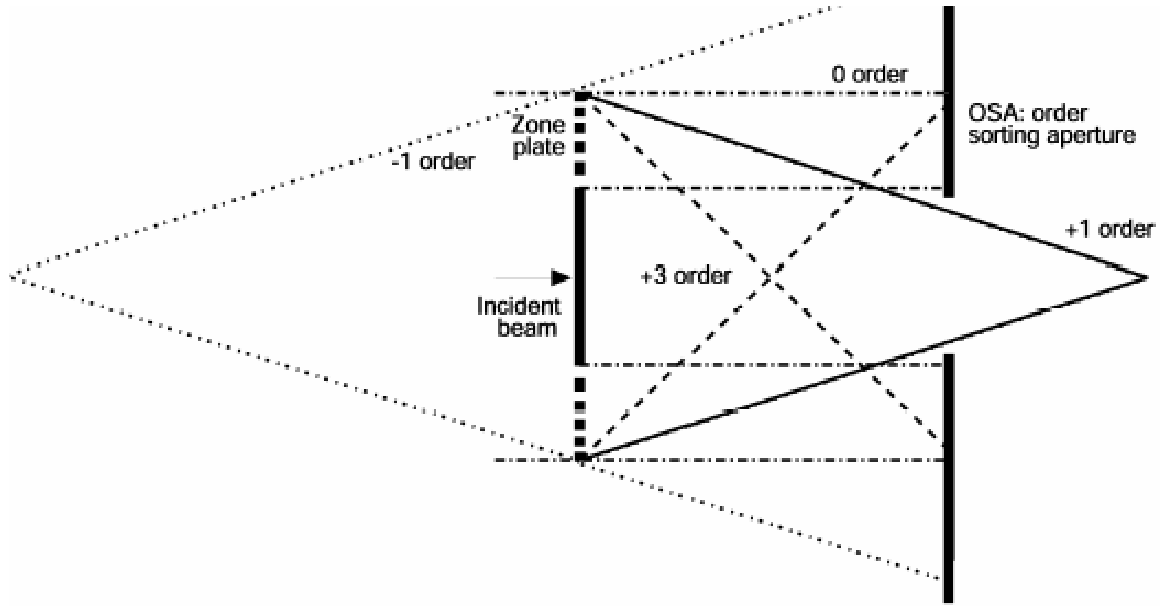
Parabolic refractive lenses

- Other efforts: cylindrical lenses by microfabrication
- Heat load not problem!
- Alignment much easier than K-B
- Chromatic
- Figure: C. G. Schroer et al., APL 82, 1485 (2003)



Zone plates

- See G. Schmahl lecture
- Central stop and Order Sorting Aperture for forming microprobe and removing other orders
- No spherical aberrations!
- But chromatic!



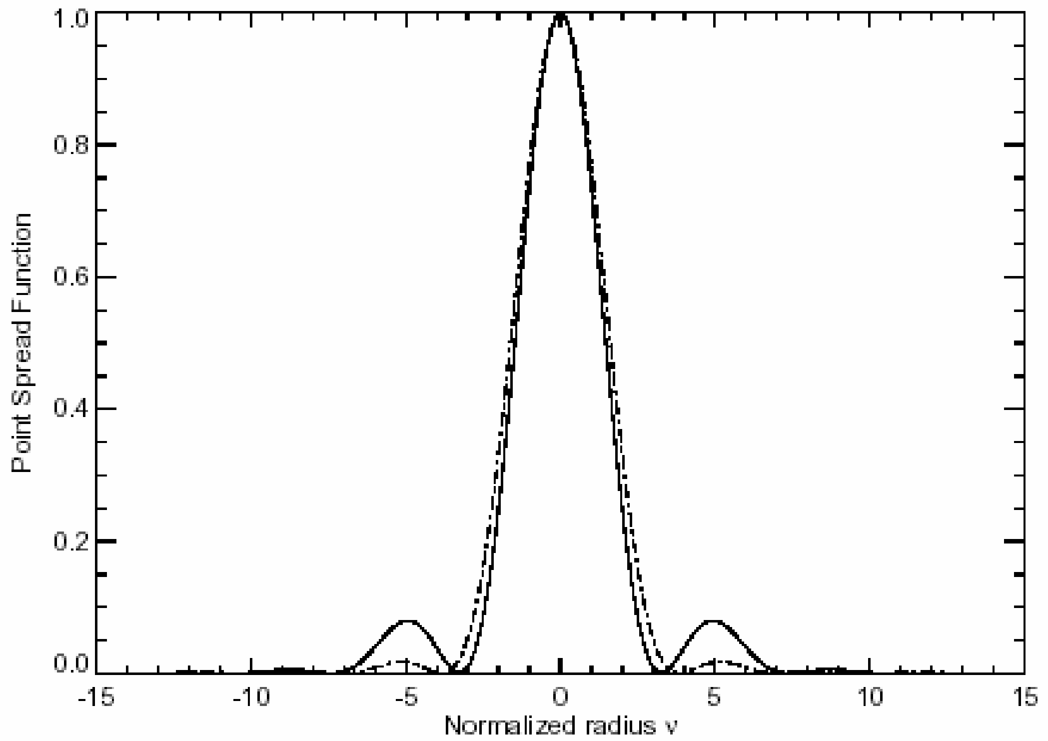
Efforts at XRADIA

- δr_n~ 100 nm, 1650 nm thick Au (for up to 24 KeV)
- δr_n~ 50 nm, <700 nm thick Au (for up to 9 KeV)
- δr_n~ 40 nm, <150 nm thick Au (for up to 1.4KeV)
- Working on achromatic X-ray lens
  – (zone plate plus non-focusing corrector)

- Mirrors and lenses demagnify small source
  - For microprobe, off-axis aberrations irrelevant!
- Diffraction-limit: focus size > λ/NA
- Strehl-ratio: What fraction of photons within focus?
- Depth of focus and working distance

Shape of focus

- Full coverage of aperture: Airy pattern
- Partial coverage (central stop, ring, segment): increased secondary rings
- Apodization



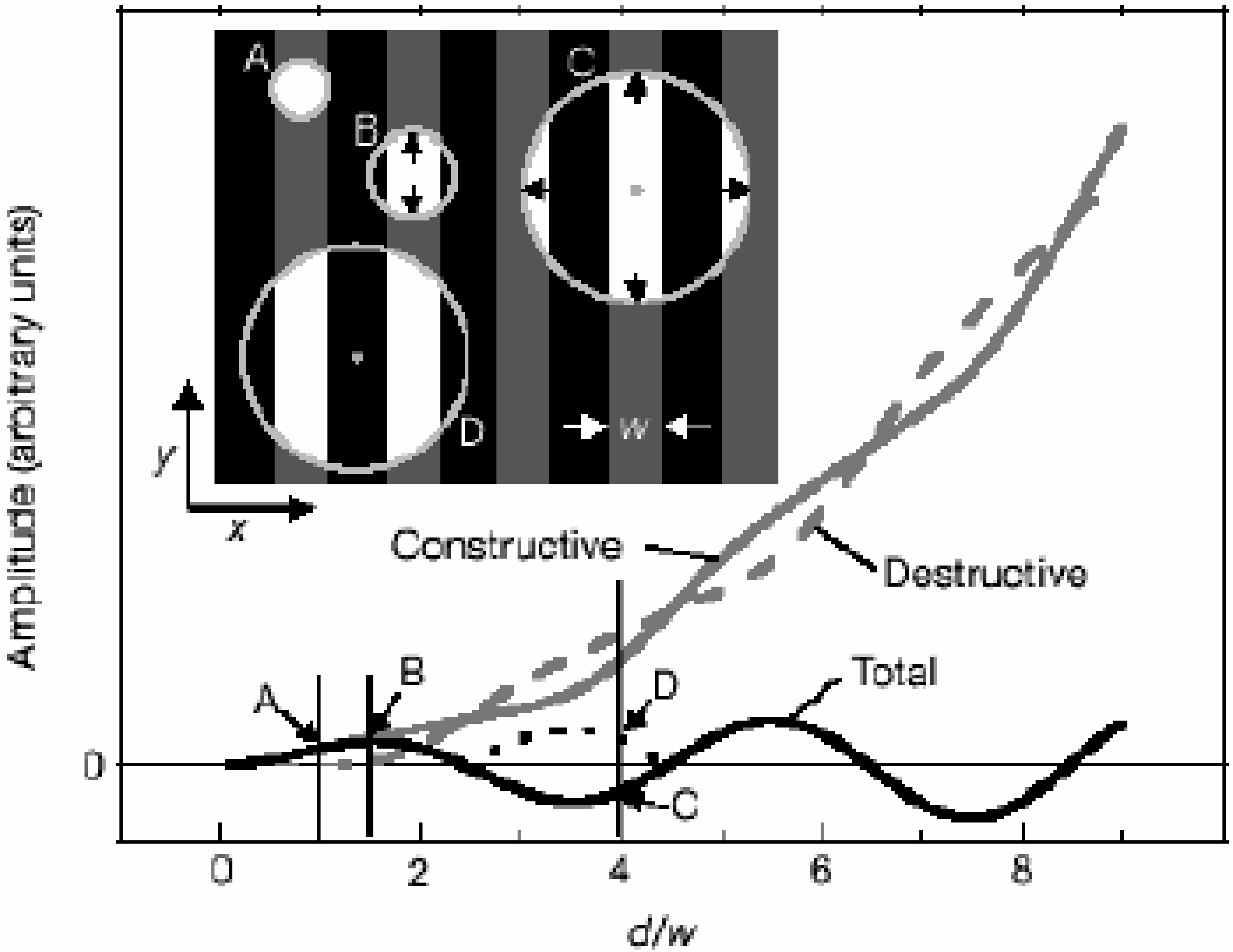
Nature 414, 184 - 188 (2001);

Sharper images by focusing soft X-rays with photon sieves

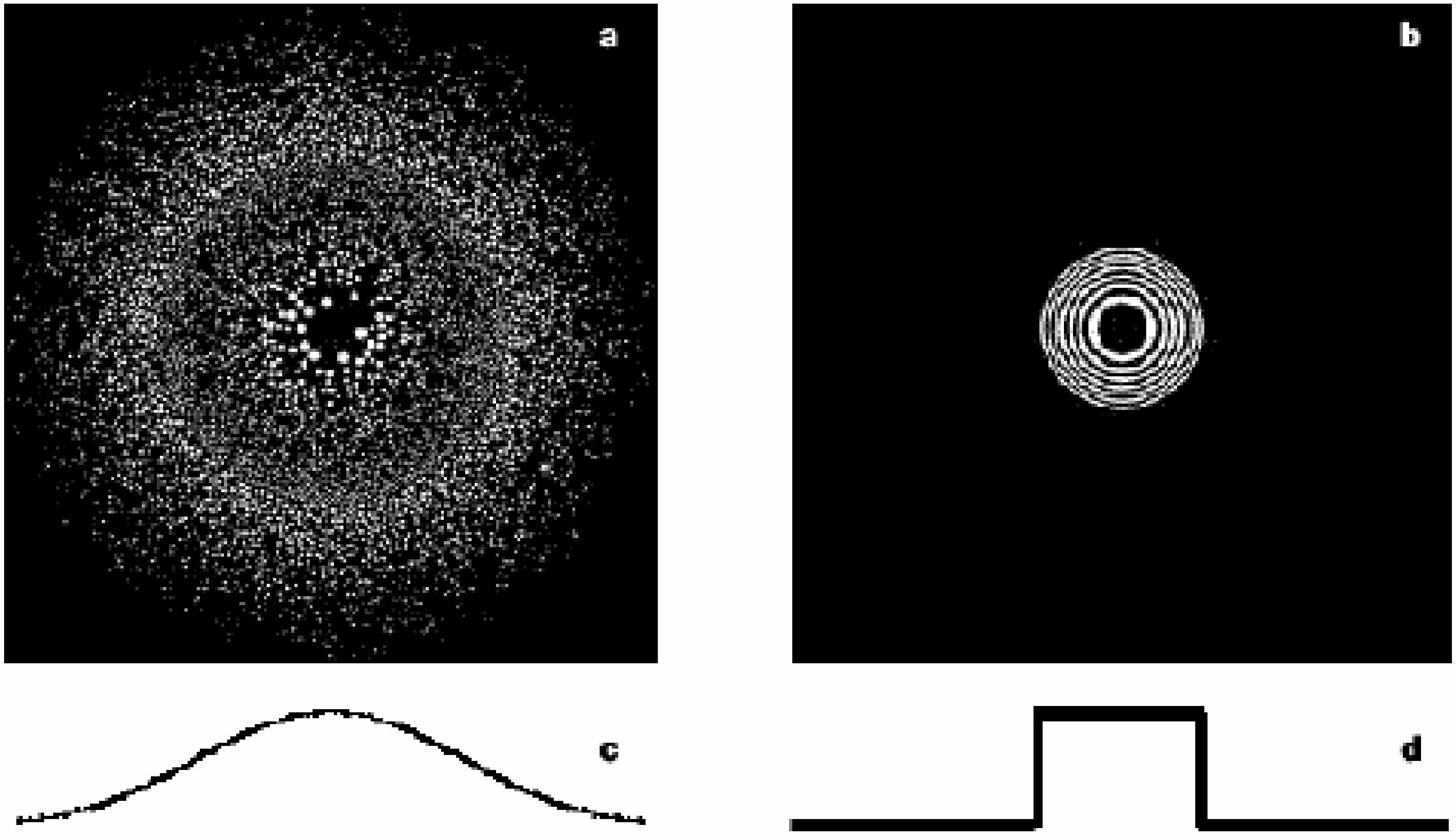
L. KIPP*, M. SKIBOWSKI*, R. L. JOHNSON†, R. BERNDT*, R. ADELUNG*, S. HARM* & R. SEEMANN‡

* Institut für Experimentelle und Angewandte Physik, Universität Kiel, D-24098 Kiel, Germany
† Institut für Experimentalphysik, Universität Hamburg, D-22761 Hamburg, Germany
‡ Niedmers & Seemann, **European Patent Attorneys**, D-22767 Hamburg, Germany

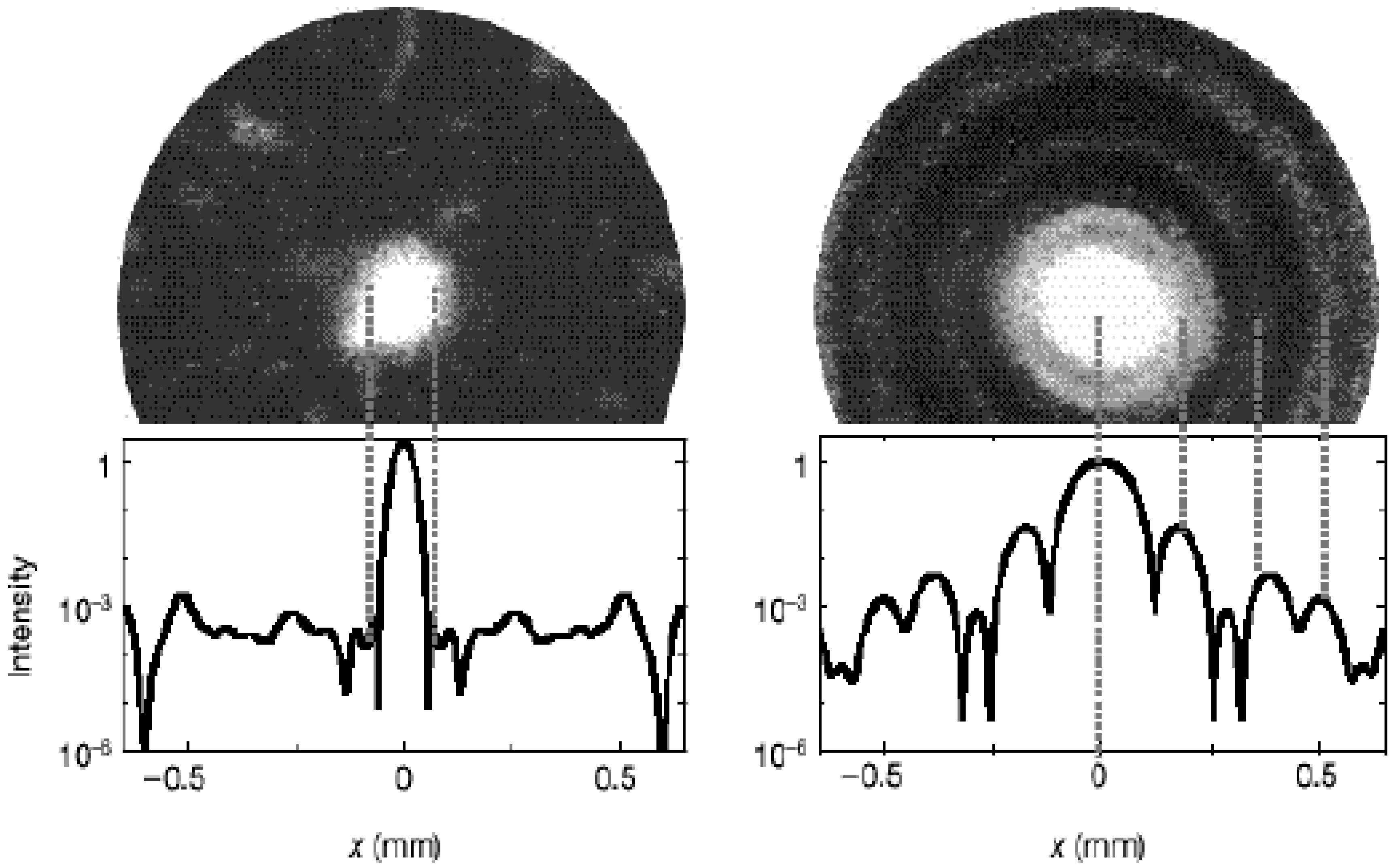
Fresnel zone plates consisting of alternating transmissive and opaque circular rings can be used to focus X-rays1. The spatial resolution that can be achieved with these devices is of the order of the width of the outermost zone and is therefore limited by the smallest structure (20–40 nm) that can be fabricated by lithography today2. Here we show that a **large number of pinholes distributed appropriately over the Fresnel zones make it possible to focus soft X-rays to spot sizes smaller than the diameter of the smallest pinhole**. In addition, **higher orders of diffraction and secondary maxima can be suppressed** by several orders of magnitude. In combination with the next generation of synchrotron light sources (free-electron lasers) these 'photon sieves' offer new opportunities for high-resolution X-ray microscopy and spectroscopy in physical and life sciences.



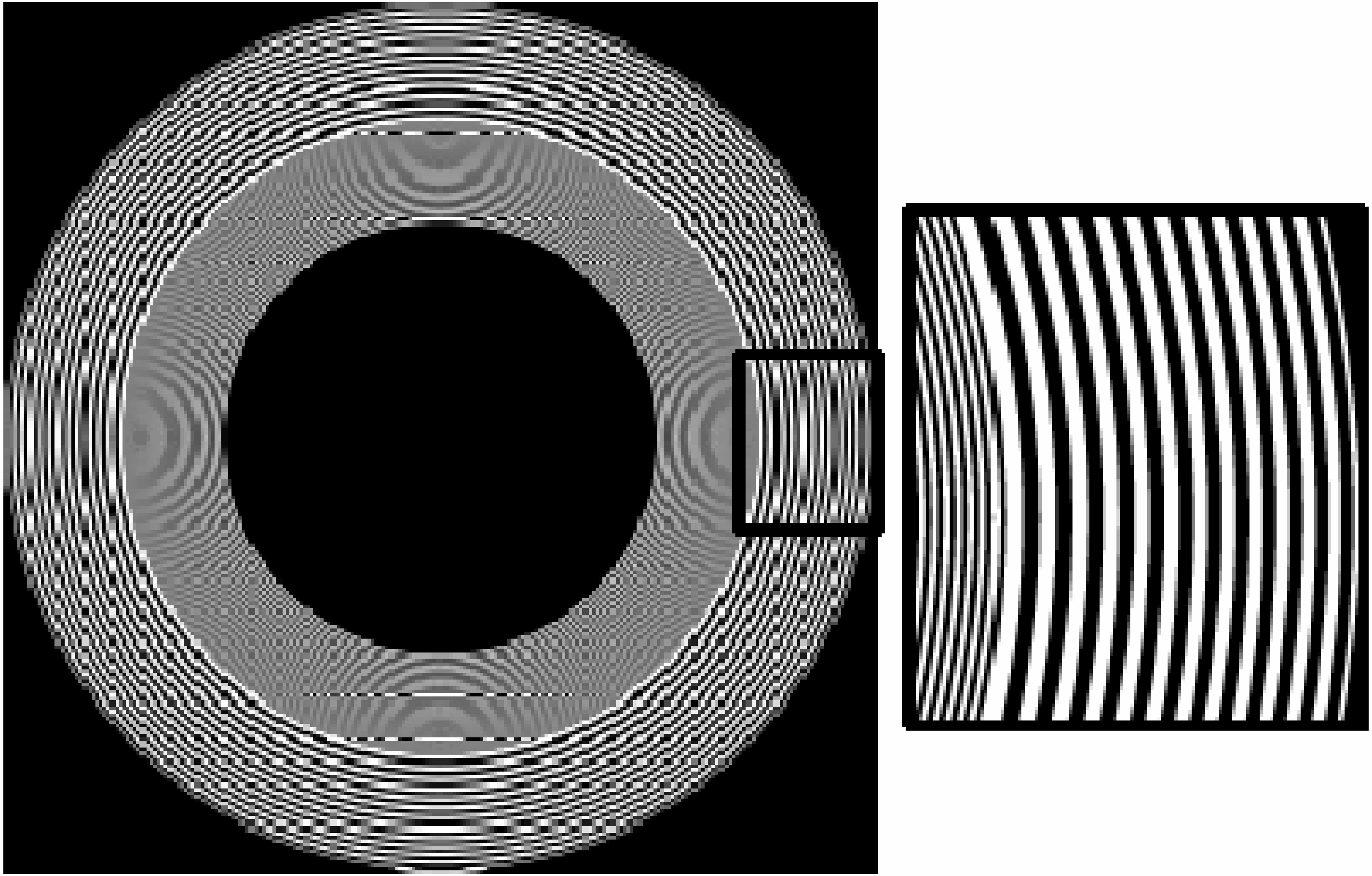
Kipp et al. Nature



Kipp et al. Nature

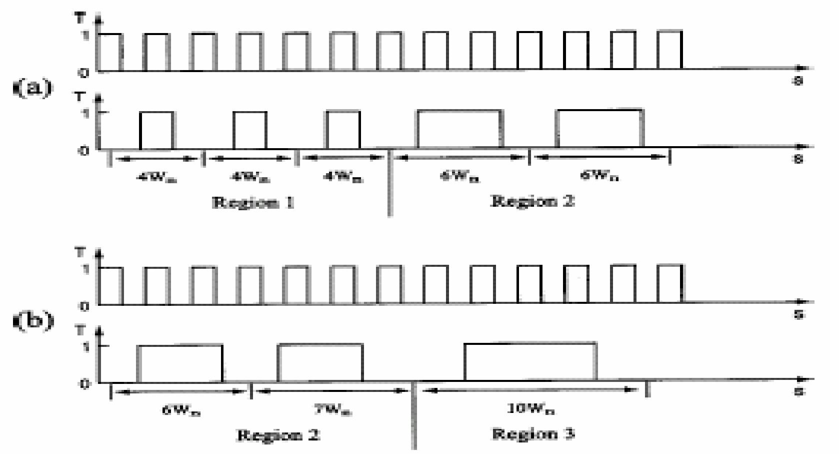


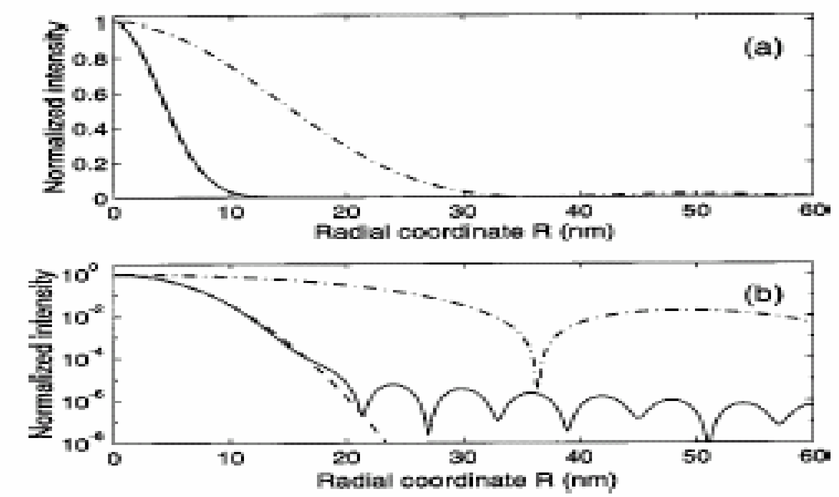
Kipp et al. Nature



Modified Fresnel zone plates that produce sharp Gaussian focal spots
Qing Cao and Juergen Jahns JOSA A20,1576 (2003)

- Optimized design using rings constrained with minimum ring-width
- Incorporates tailored transmission-filter to eliminate rings around focus
- No higher order foci
- Good efficiency (in comparison with amplitude zone plate)



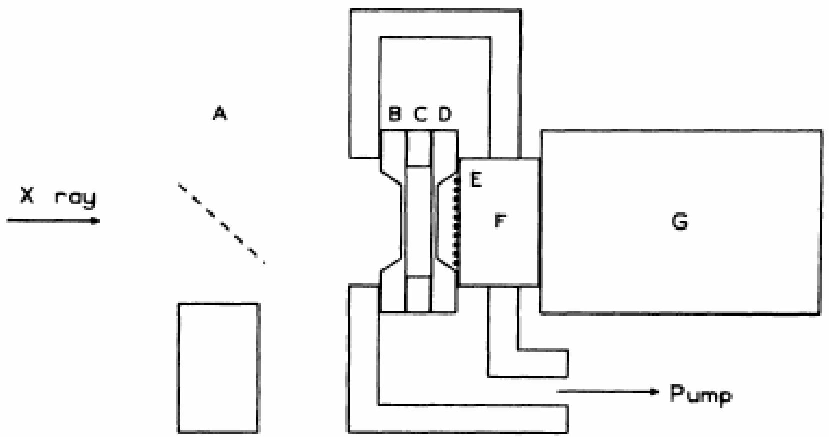


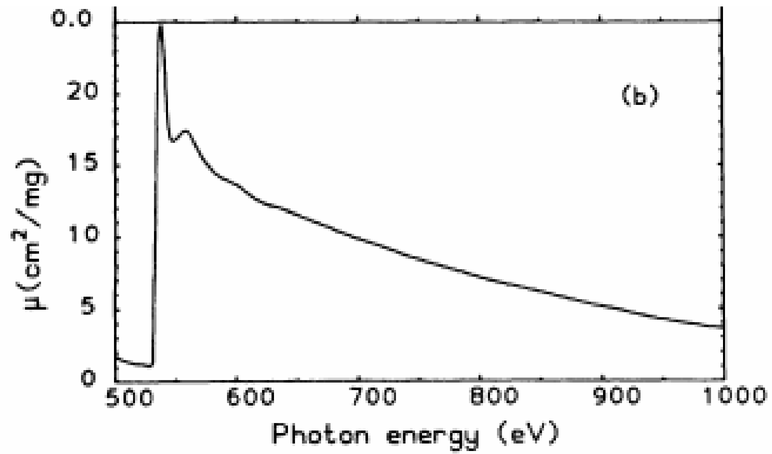
1986

Extended x-ray-absorption fine structure of liquid water

B. X. Yang and J. Kirz
Department of Physics, State University of New York at Stony Brook, Stony Brook, New York 11794
(Received 18 February 1987)

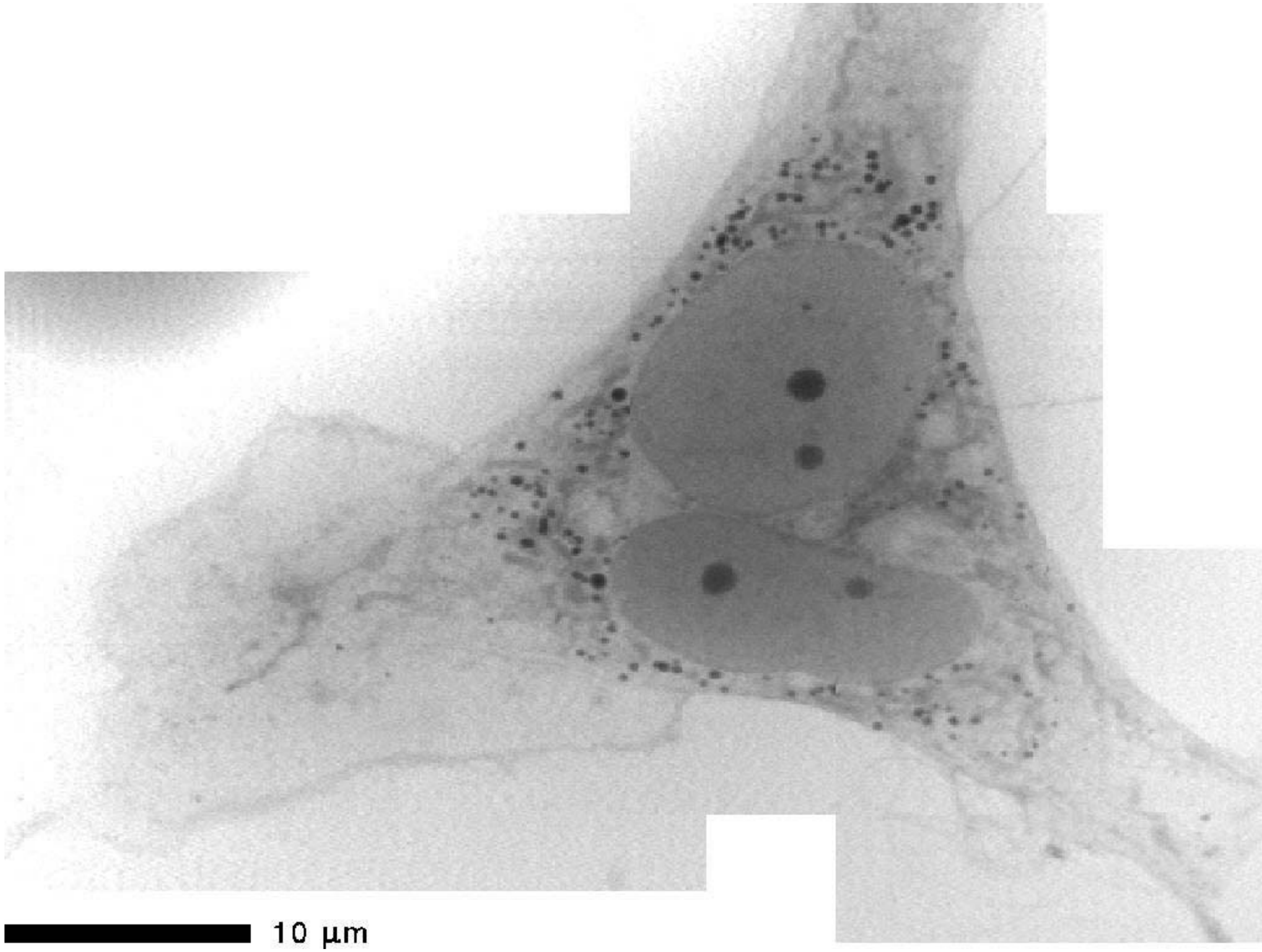
Extended x-ray-absorption fine structure (EXAFS) of liquid water above the oxygen *K* edge is reported for the first time. Major features of the EXAFS spectrum agree with the calculated spectrum based on the known O-O pair correlation function in water. Other features are tentatively identified as due to the effect of the hydrogen atoms on the photoelectrons.





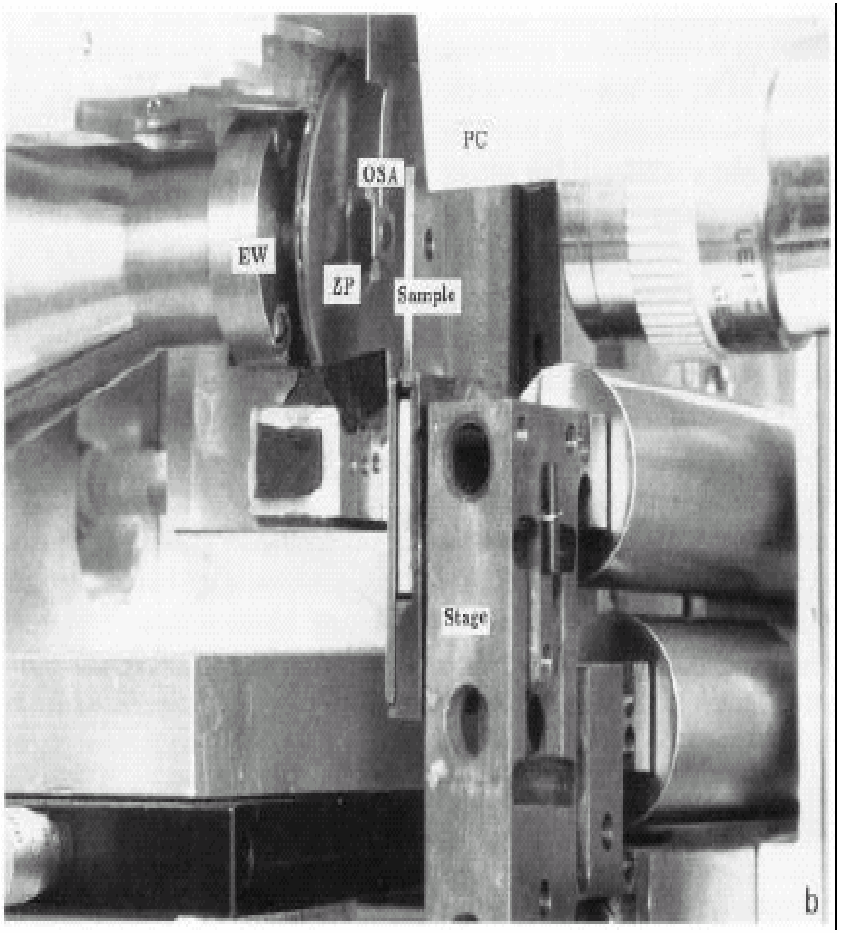
Phys Rev B 36, 1361 ('87)

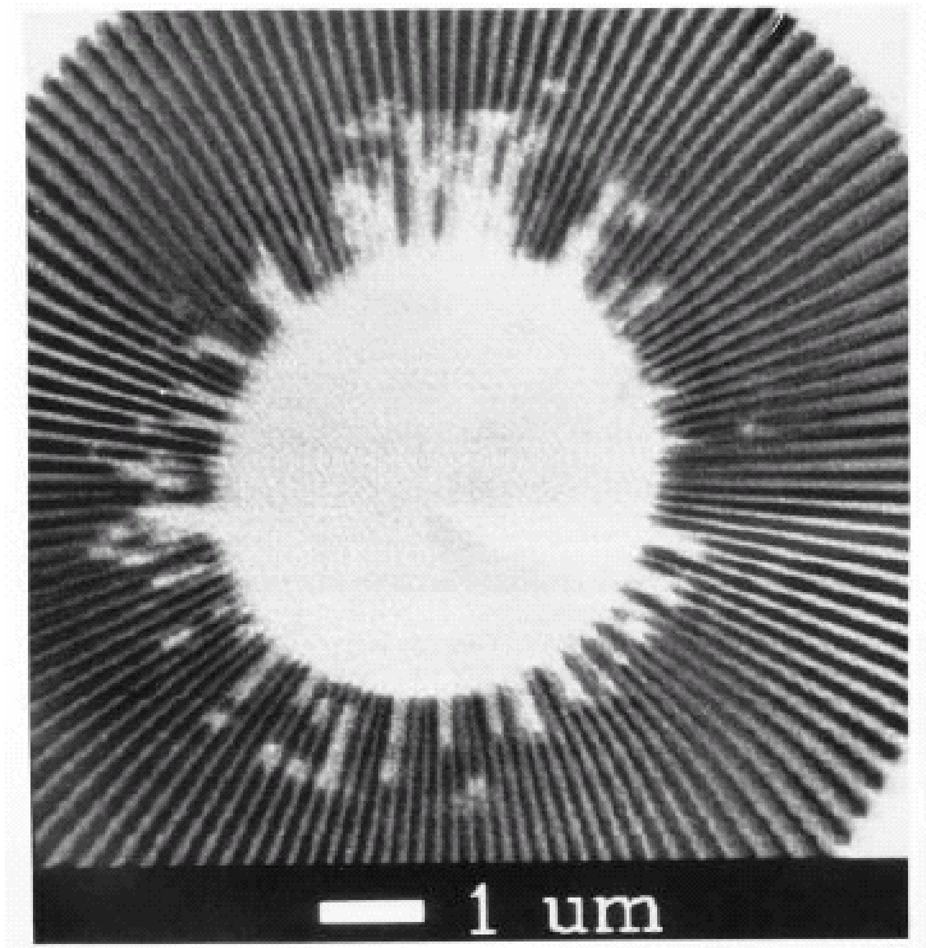
STXM – wet specimens 1986



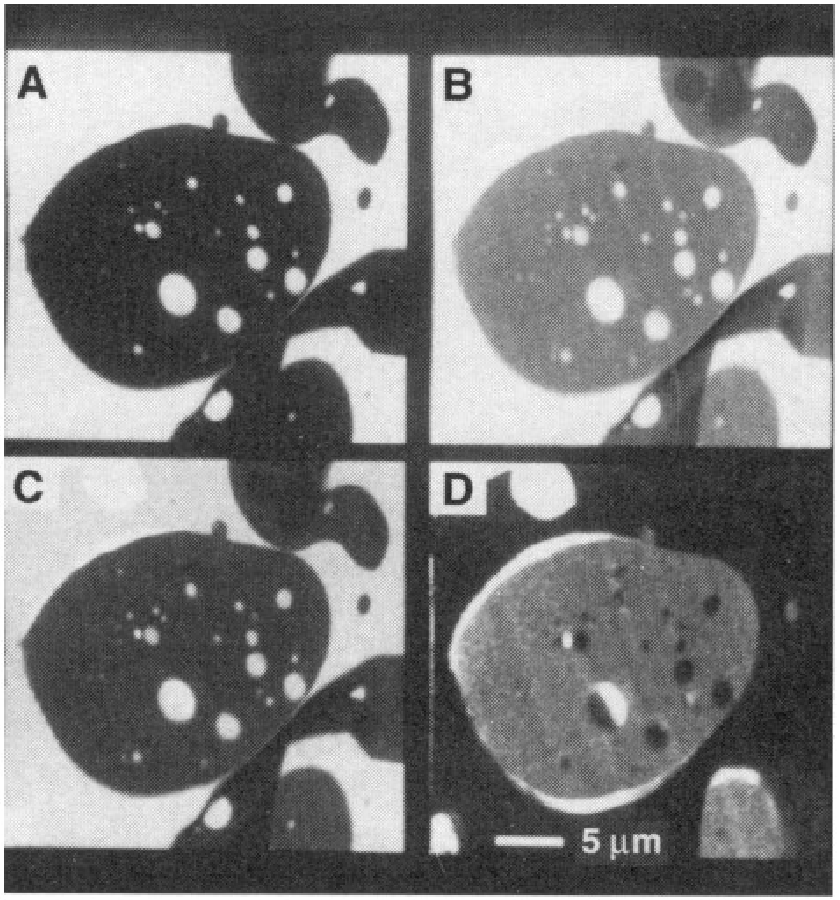
Gilbert thesis, '92

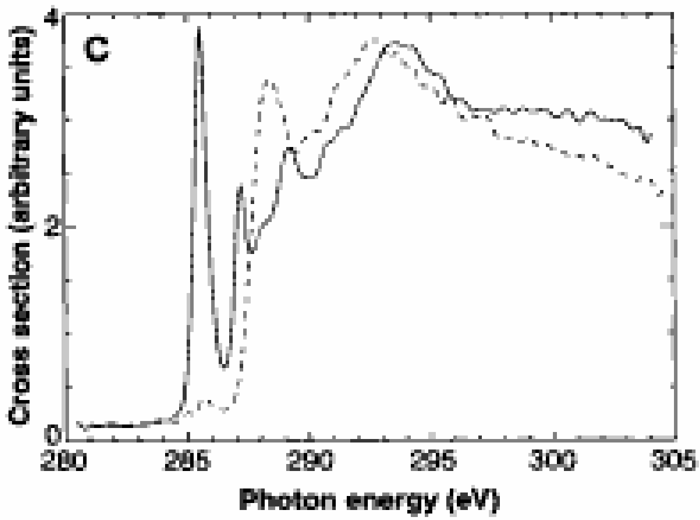
C. Jacobsen et al., Opt. Comm. 86, 351 (1991)
45 nm zone plate made at IBM/CXRO
X1 undulator, 340 eV





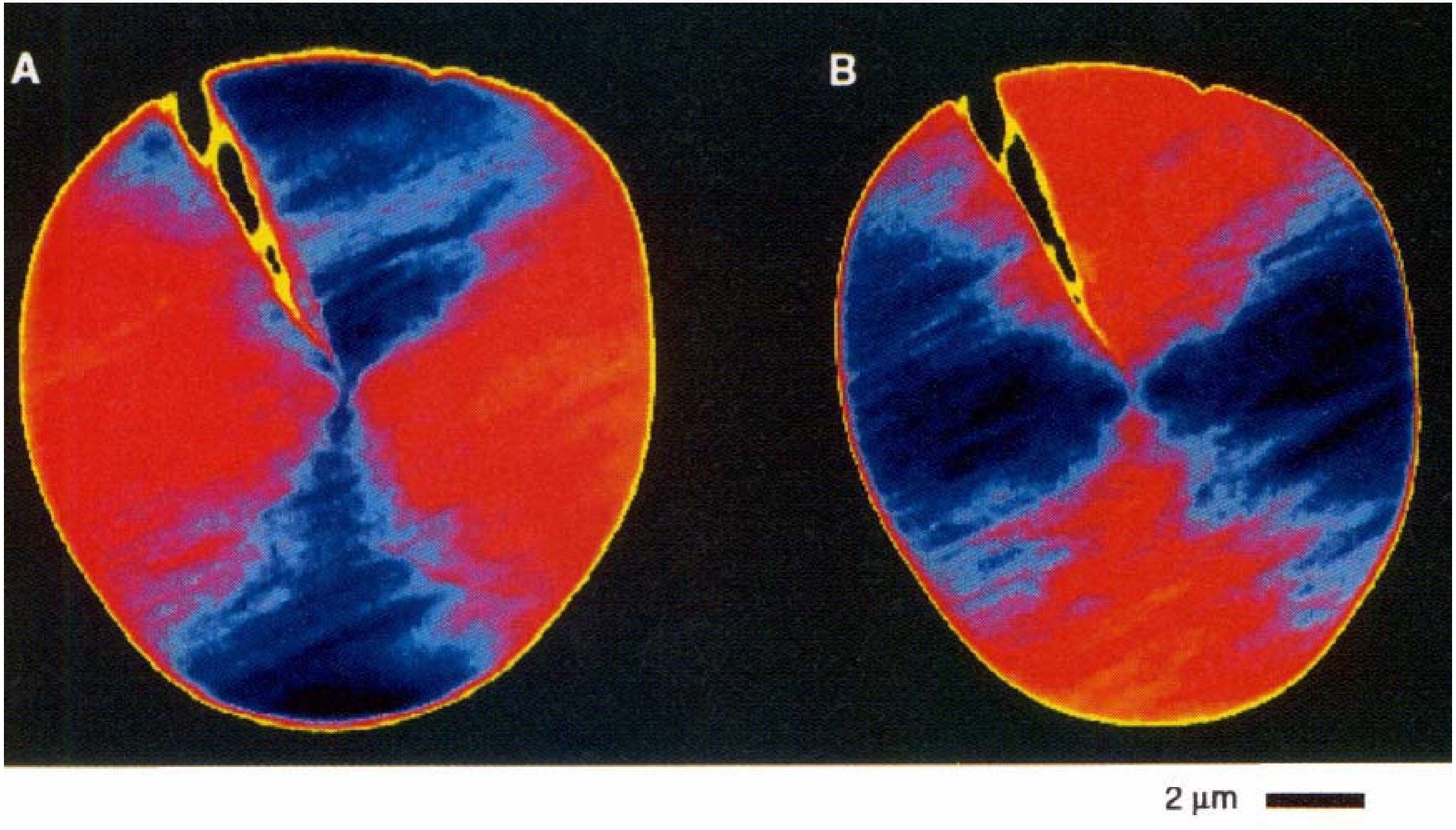
STXM 1992
spectromicroscopy





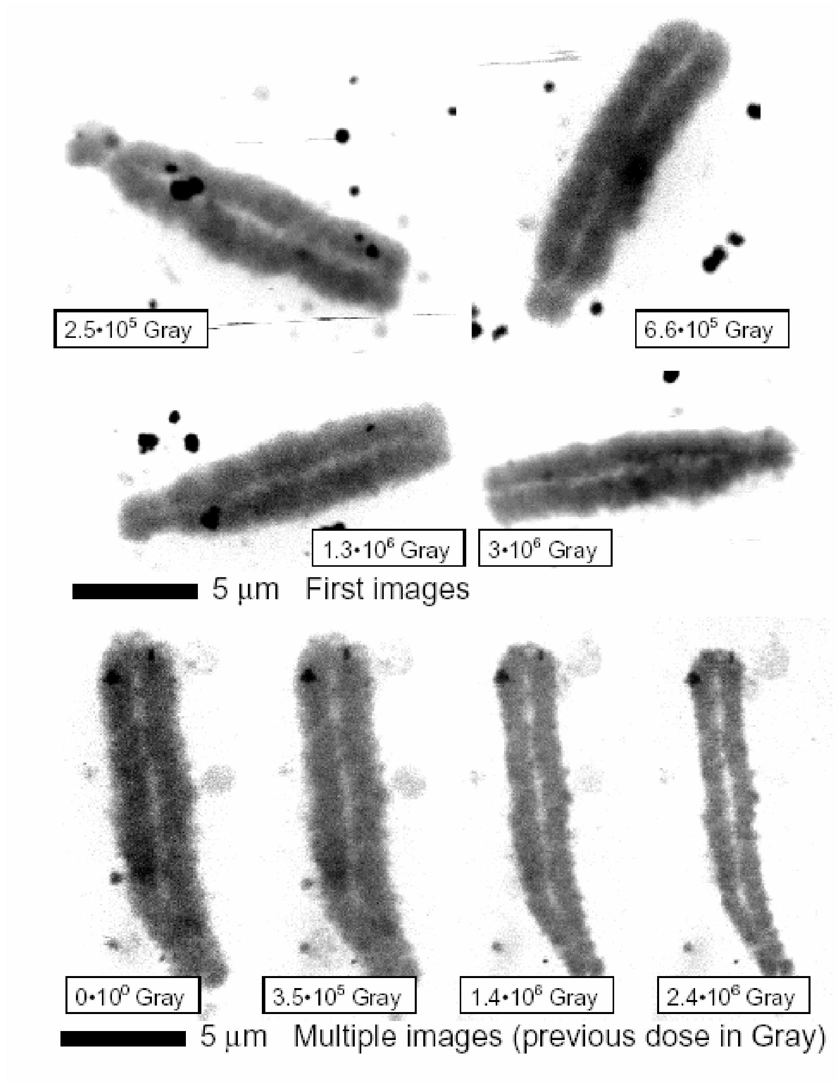
Ade et al. Science

Linear dichroism microscopy Ade & Hsiao, NSLS 1993



Ade & Hsiao, Science 1993

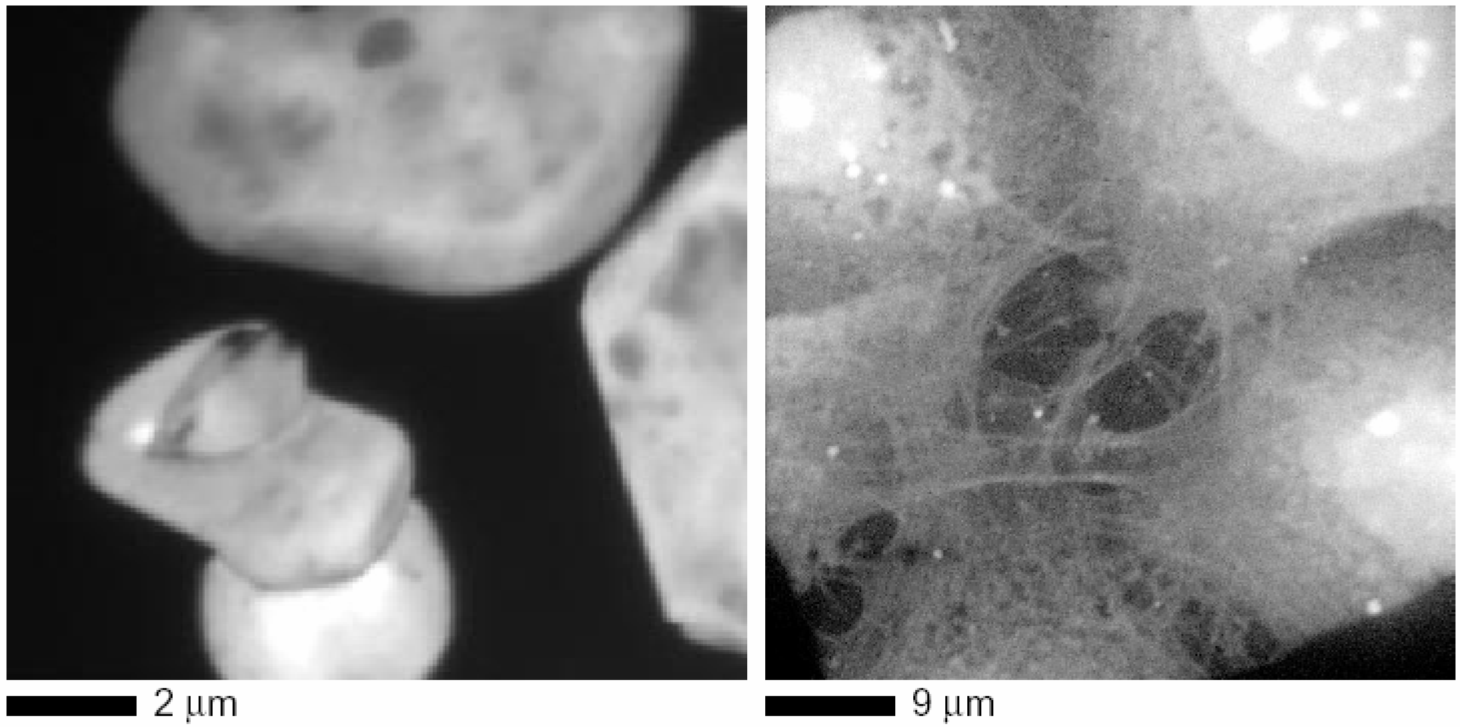
Radiation damage studies, 1993



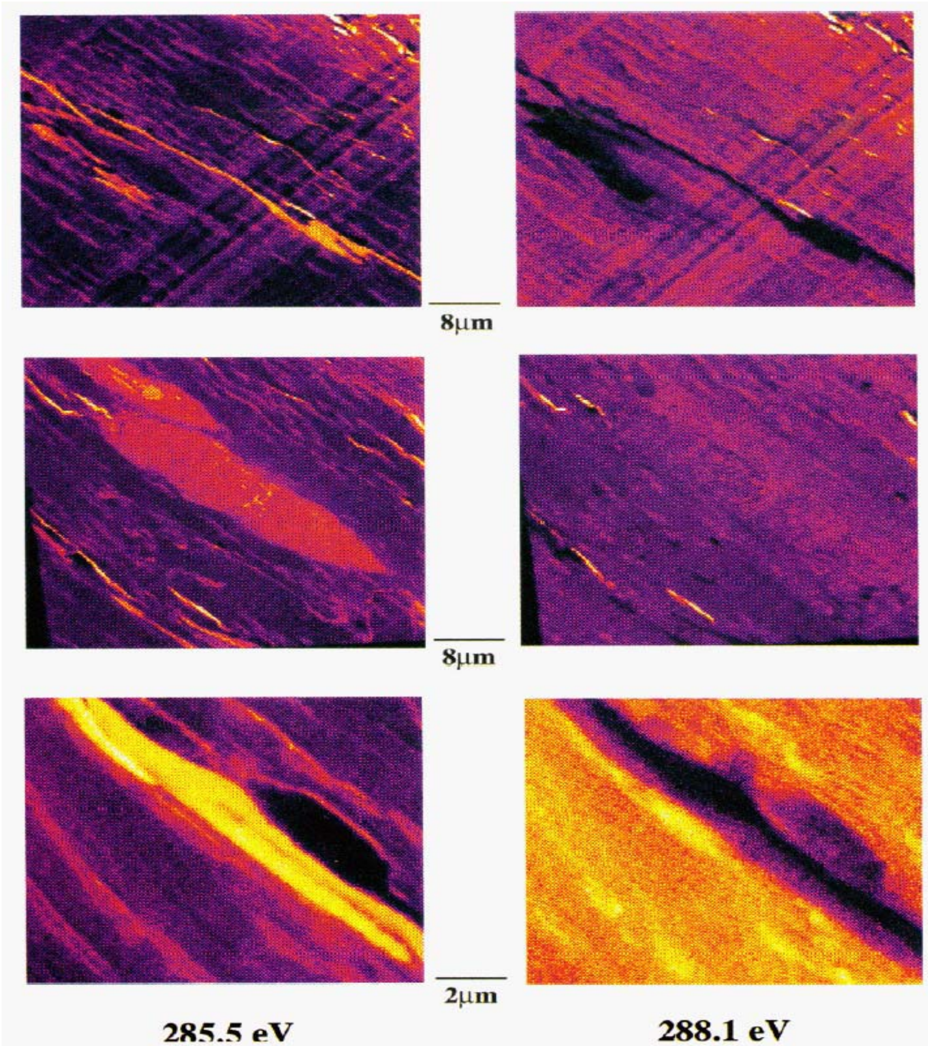
Williams et al. J. Microsc

Visible light detection:SLXM

phosphor grains 1993   actin filaments 1994

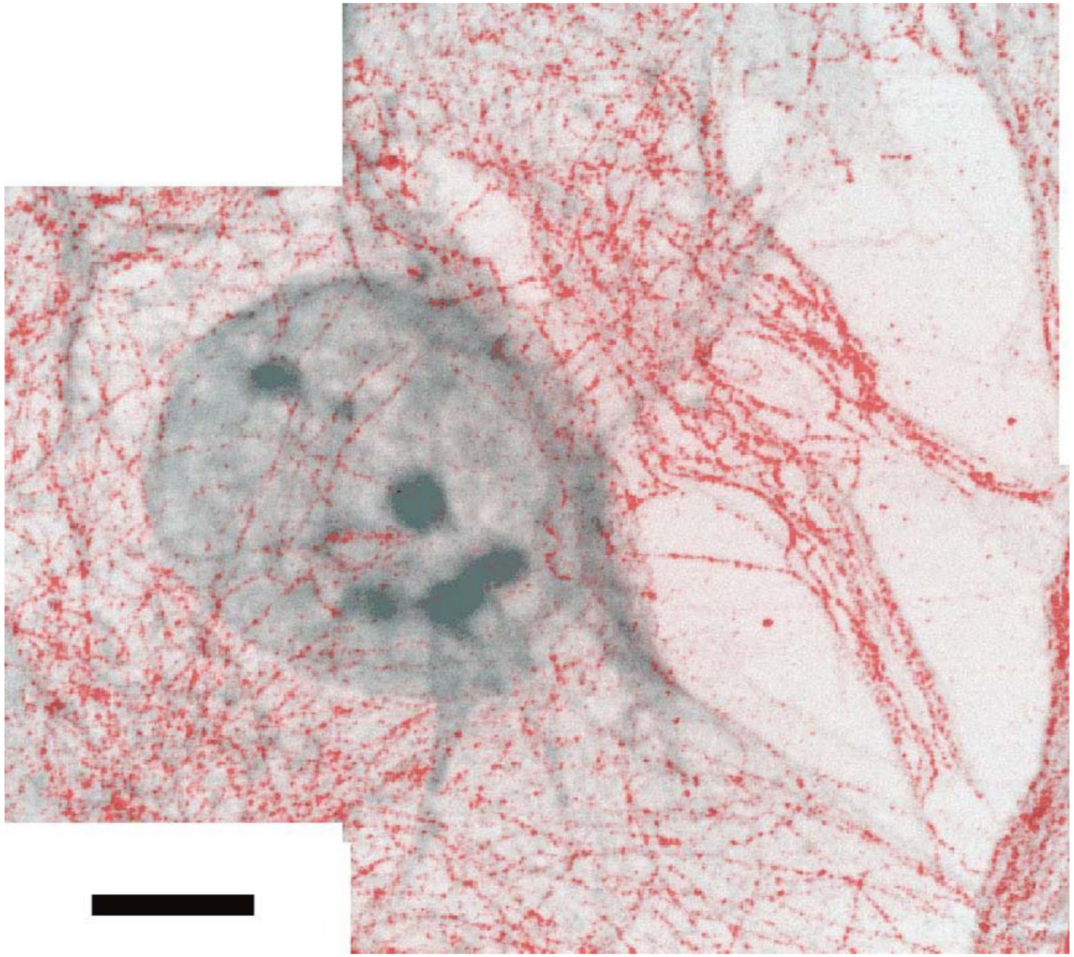


Environmental/Earth Science 1994
diagenesis of coal



Botto, Cody,... Energy&Fuels

Gold labeled specimens 1996

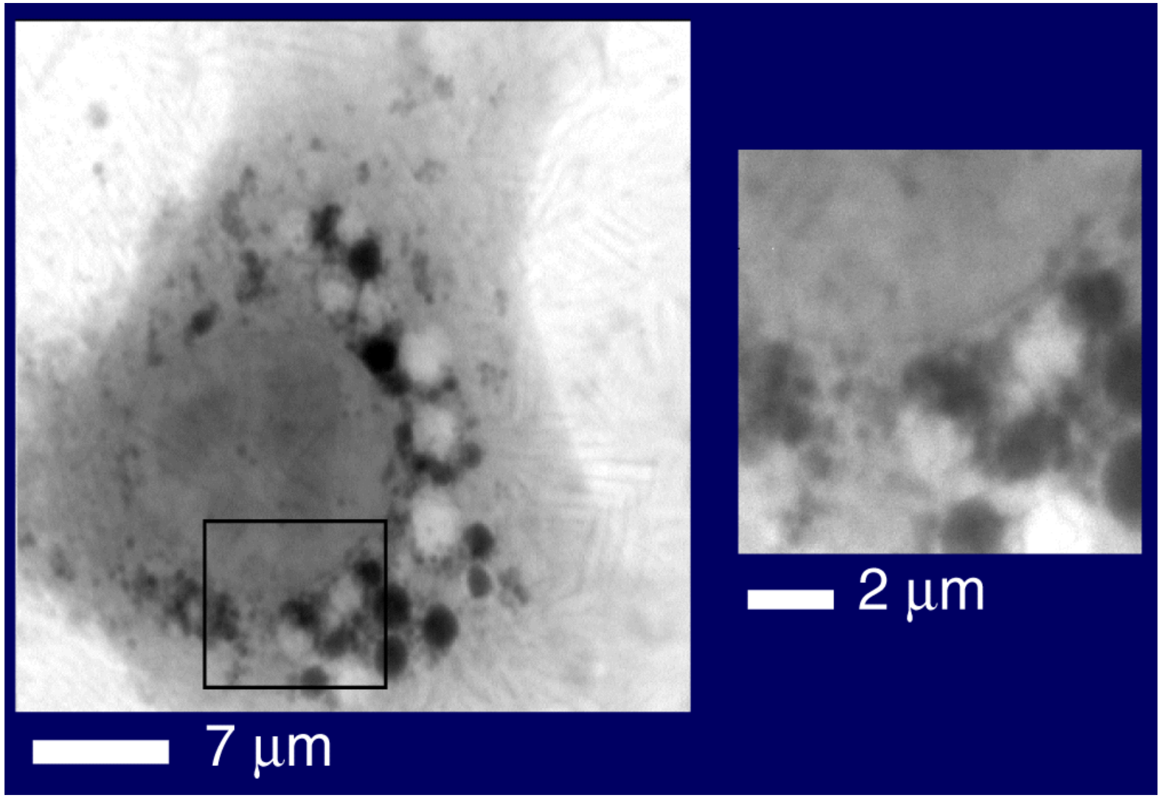


Chapman et al. J. Micr. Soc. Am
scale bar 7 microns

Cryo-STXM: Frozen-hydrated Fibroblasts 1999

Grids with live cells are

- Taken from culture medium and blotted
- Plunged into liquid ethane (cooled by liquid nitrogen)
- Loaded into cryo holder

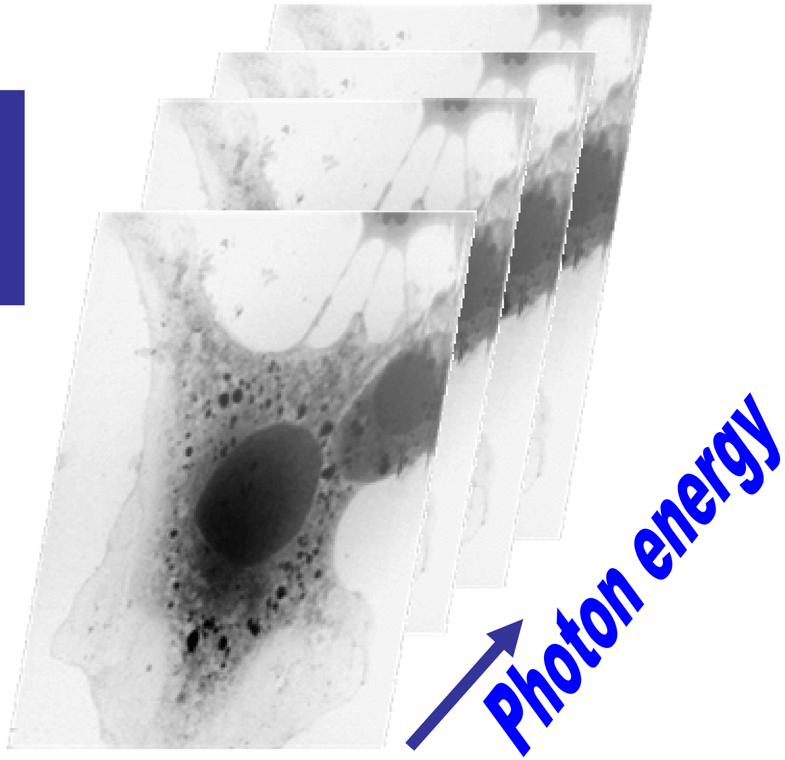


Spectromicroscopy by image stacks 1999

- Acquire sequence of images over XANES spectral region; automatically align using Fourier cross-correlations; extract spectra.

Images at N=150 energies are common.

IDL-based analysis tools are made available



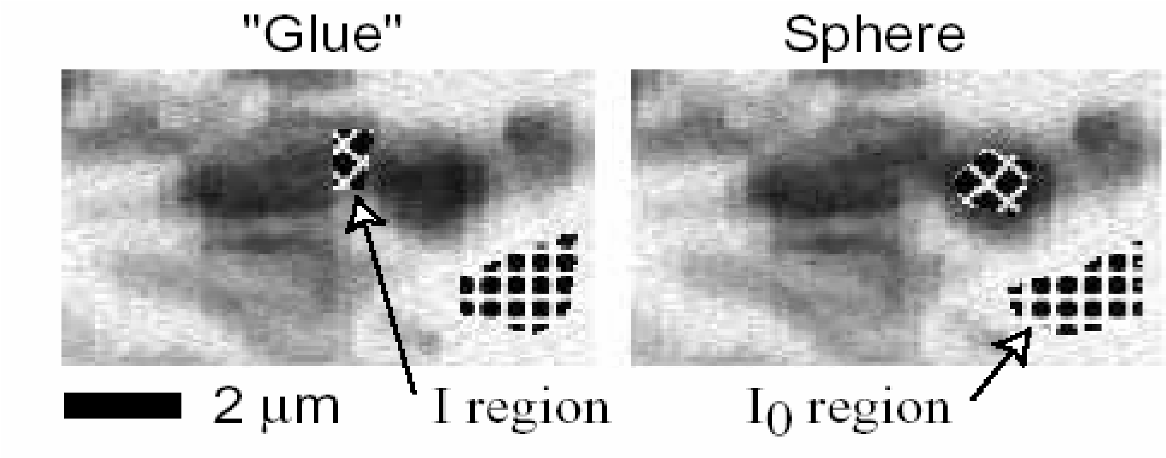
Jacobsen et al., J. Microsc. 2000

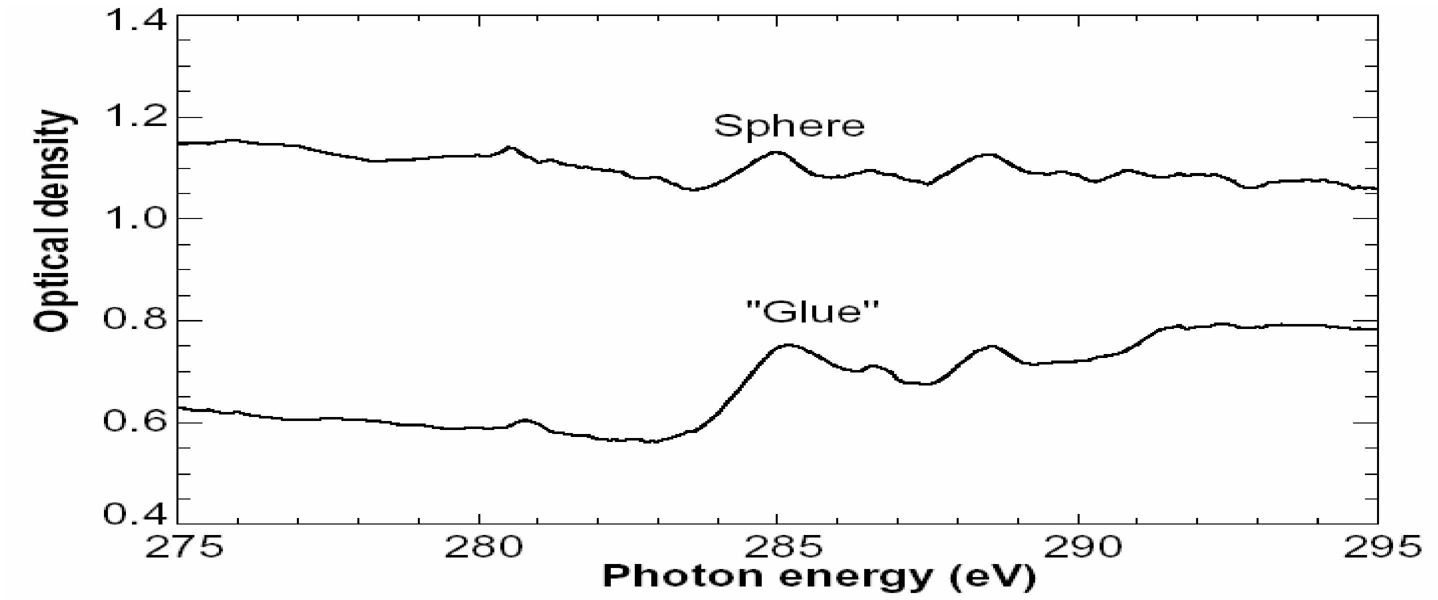
Analysis of stacks

C. Jacobsen and students

- Singular Value Decomposition
  - (components and model spectra known)
- Principal Component Analysis
  - (components unknown)
- Cluster analysis

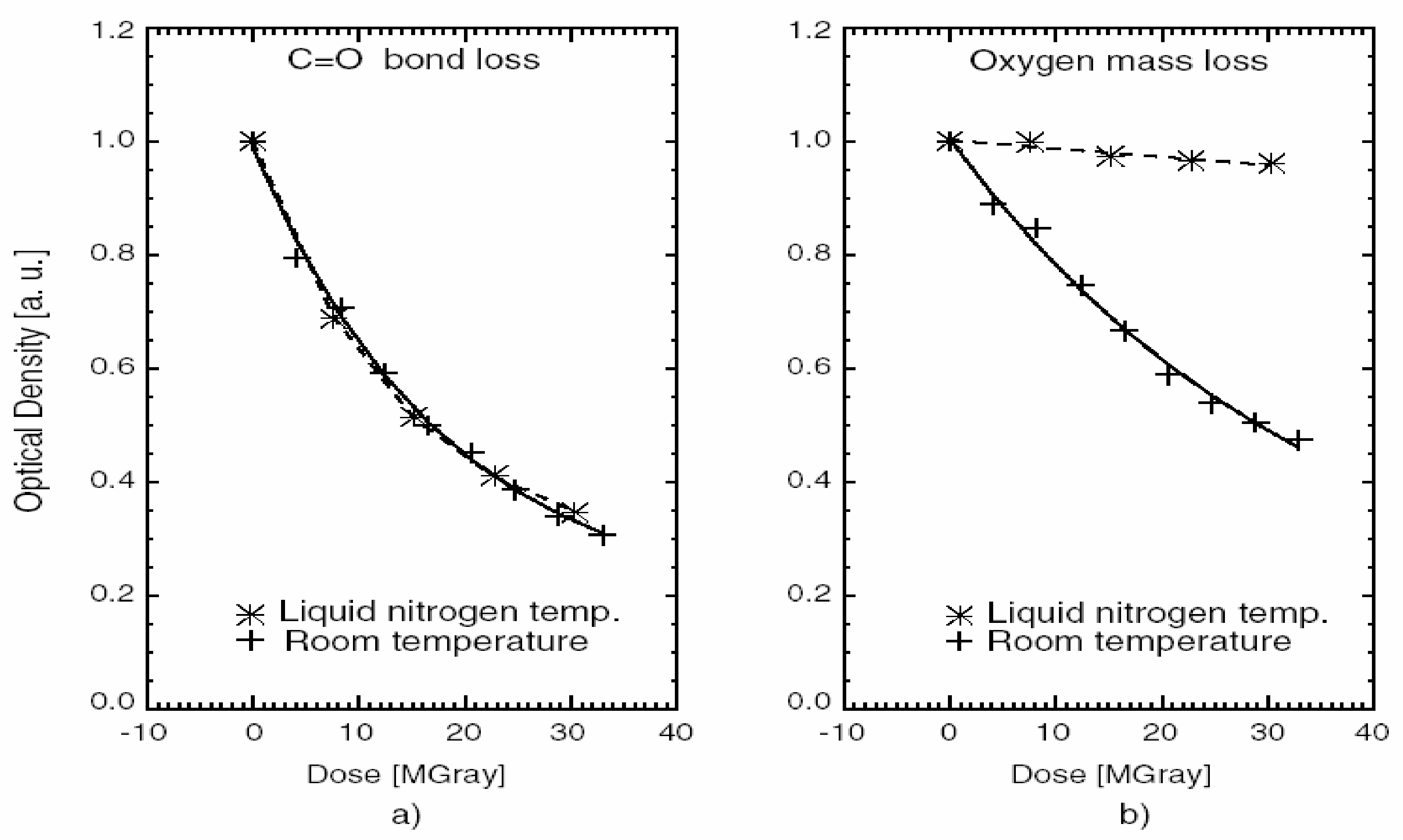
Spectra from selected areas: lower radiation dose





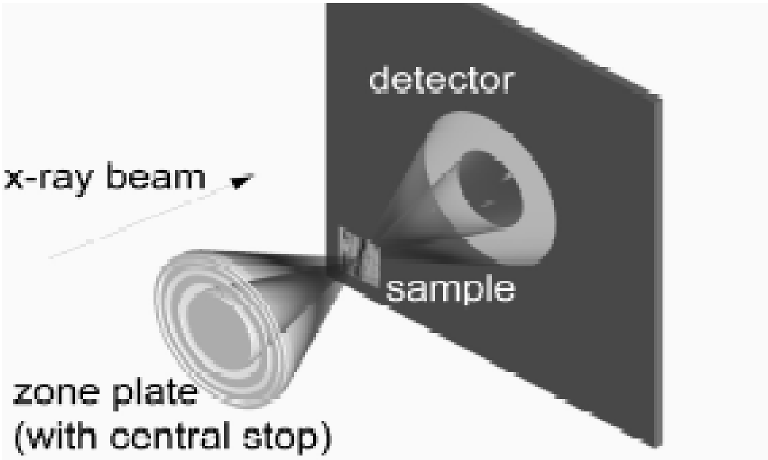
Jacobsen et al., J. Microsc. 2000.

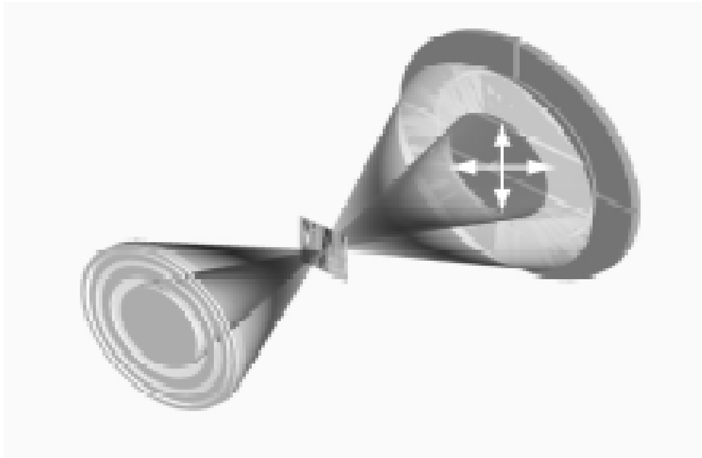
Cryo protects PMMA against mass loss, but not against chemical change!

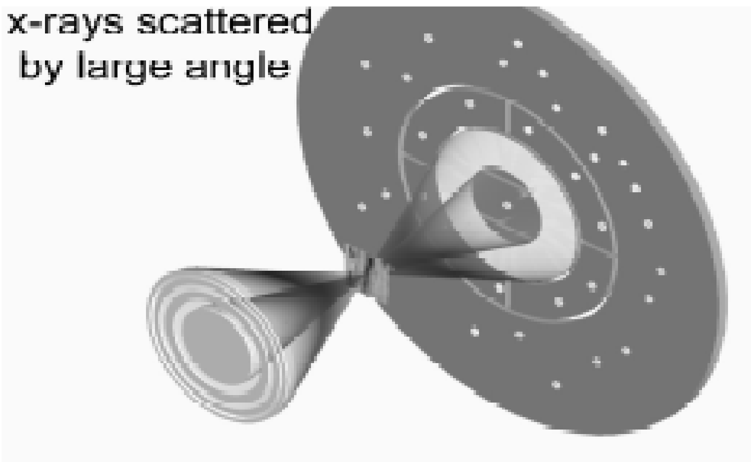


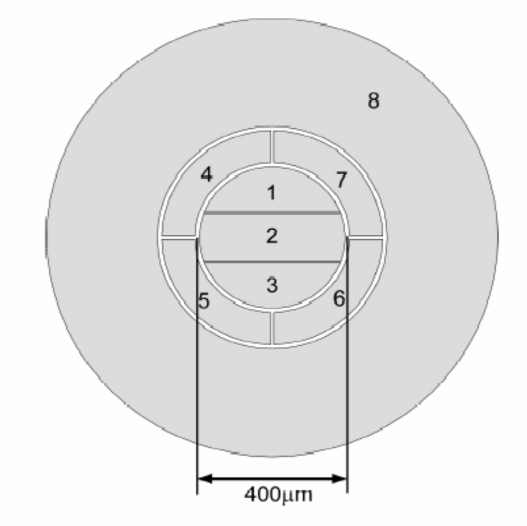
Beetz & Jacobsen, J. Synch. Rad. 2003

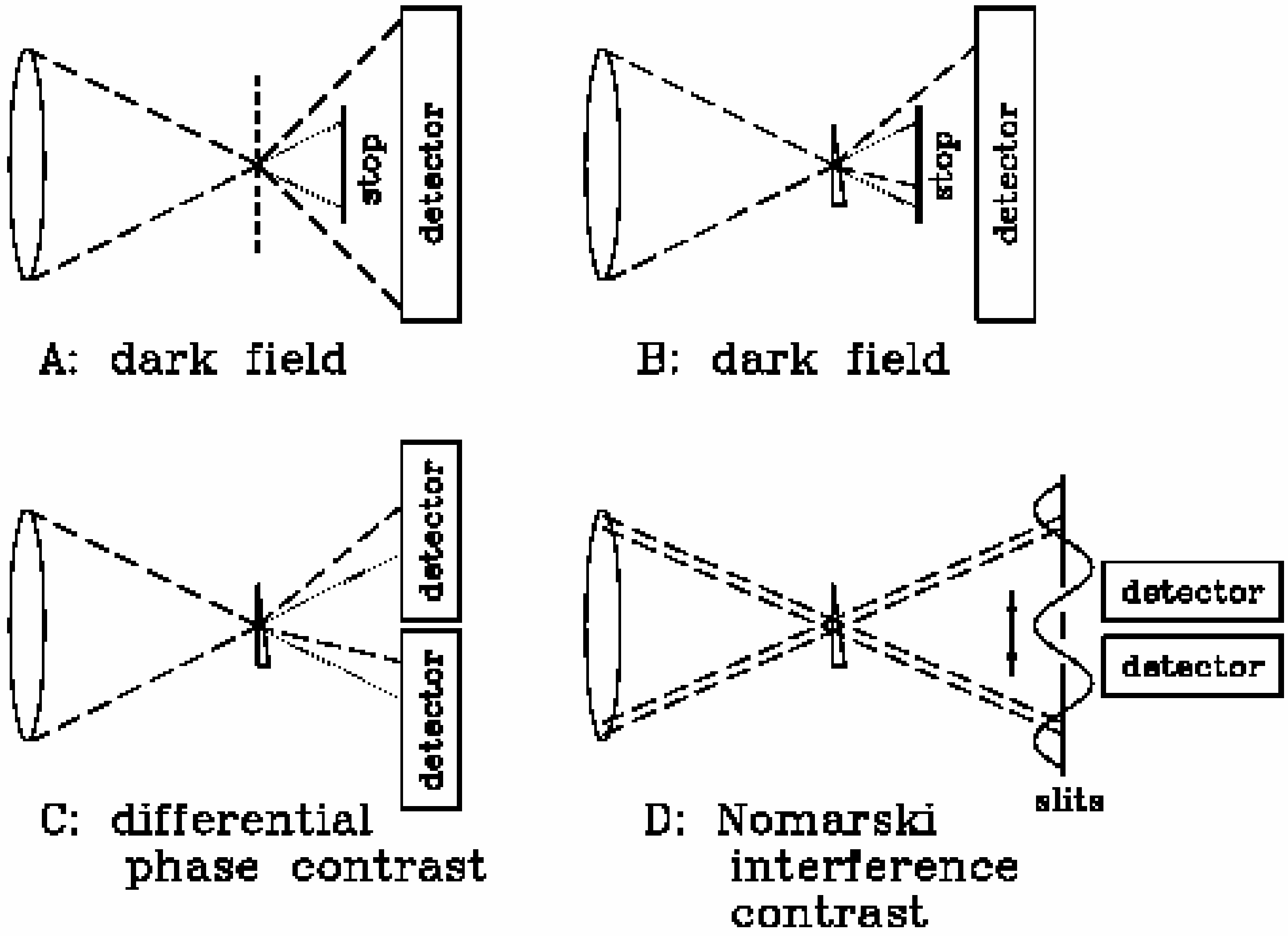
segmented detector 2001 (Stony Brook, BNL Instrumentation)







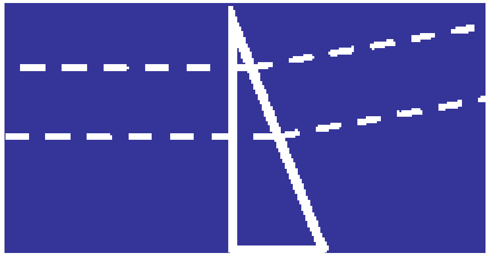




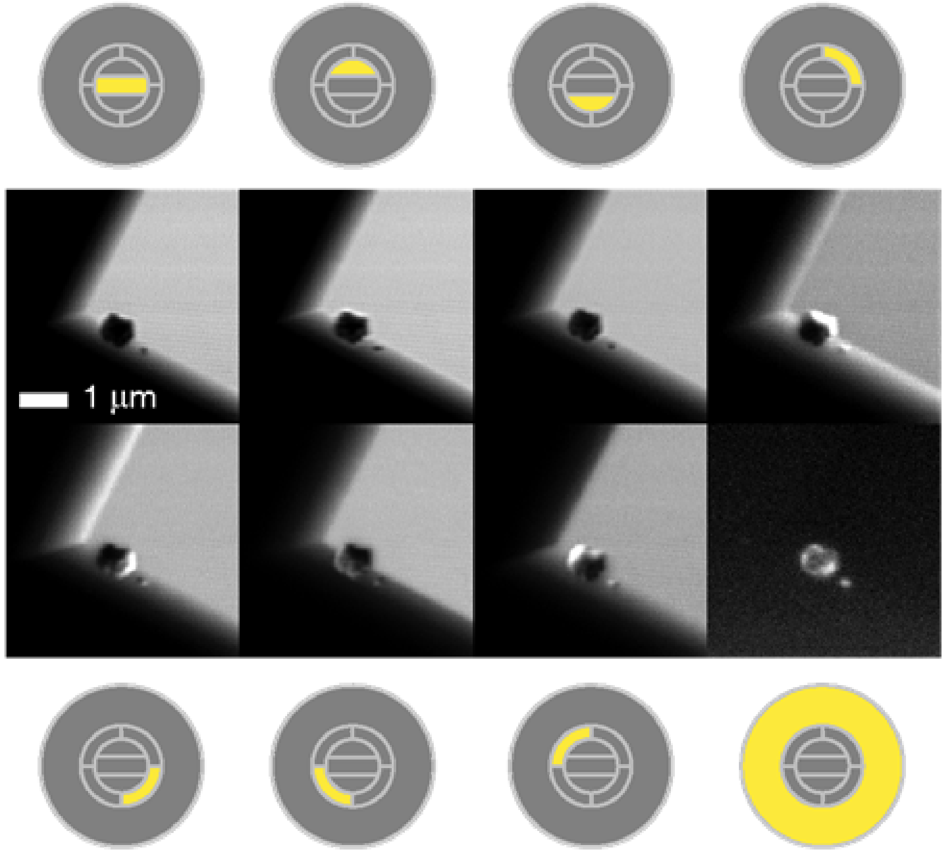
Kirz et al. QRB

Segmented silicon drift detector

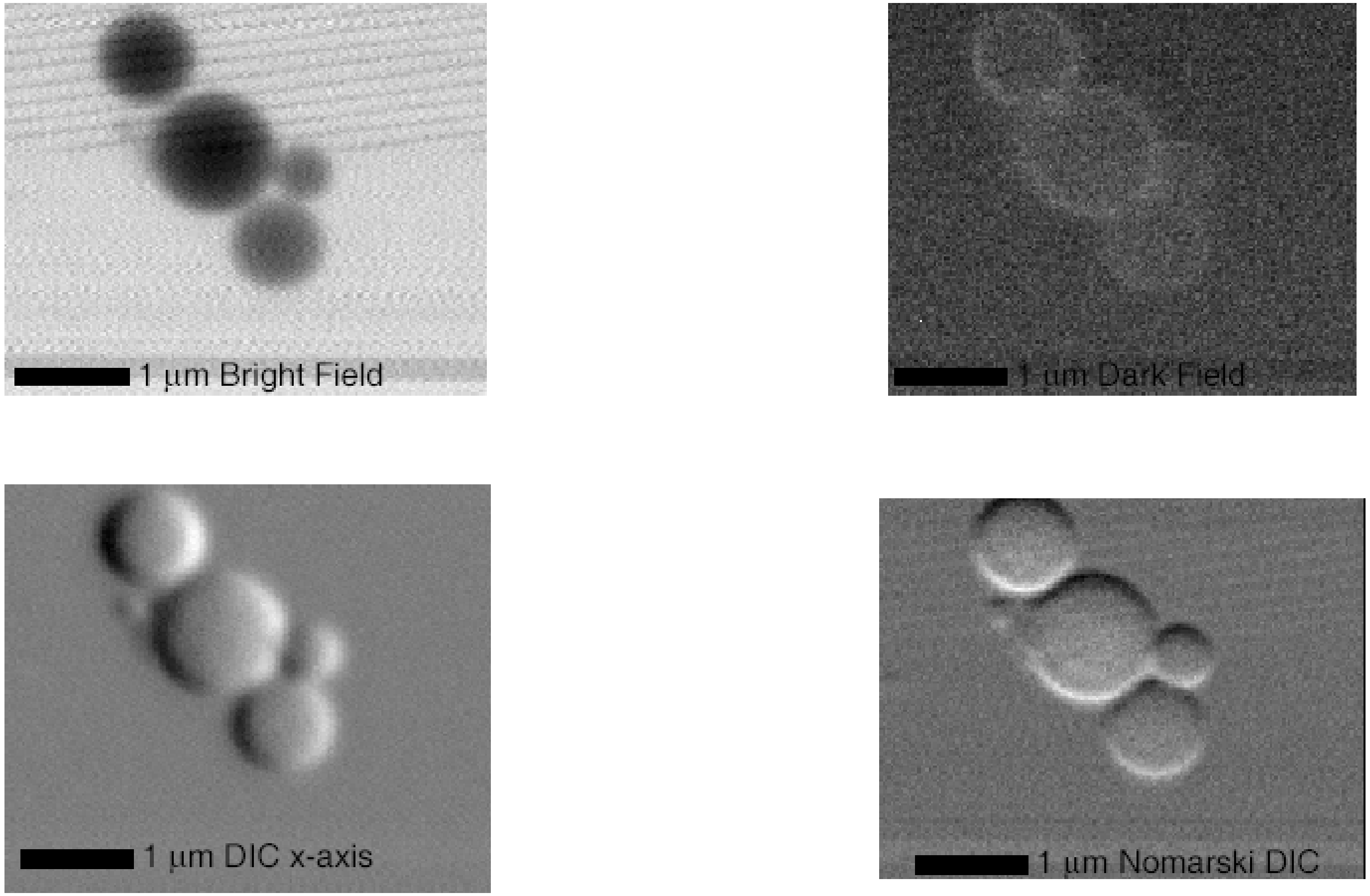
- Corner of silicon nitride window: silicon at ~54° wall slope forms a prism
- Refraction of x-ray beam in *opposite* direction from visible light prisms



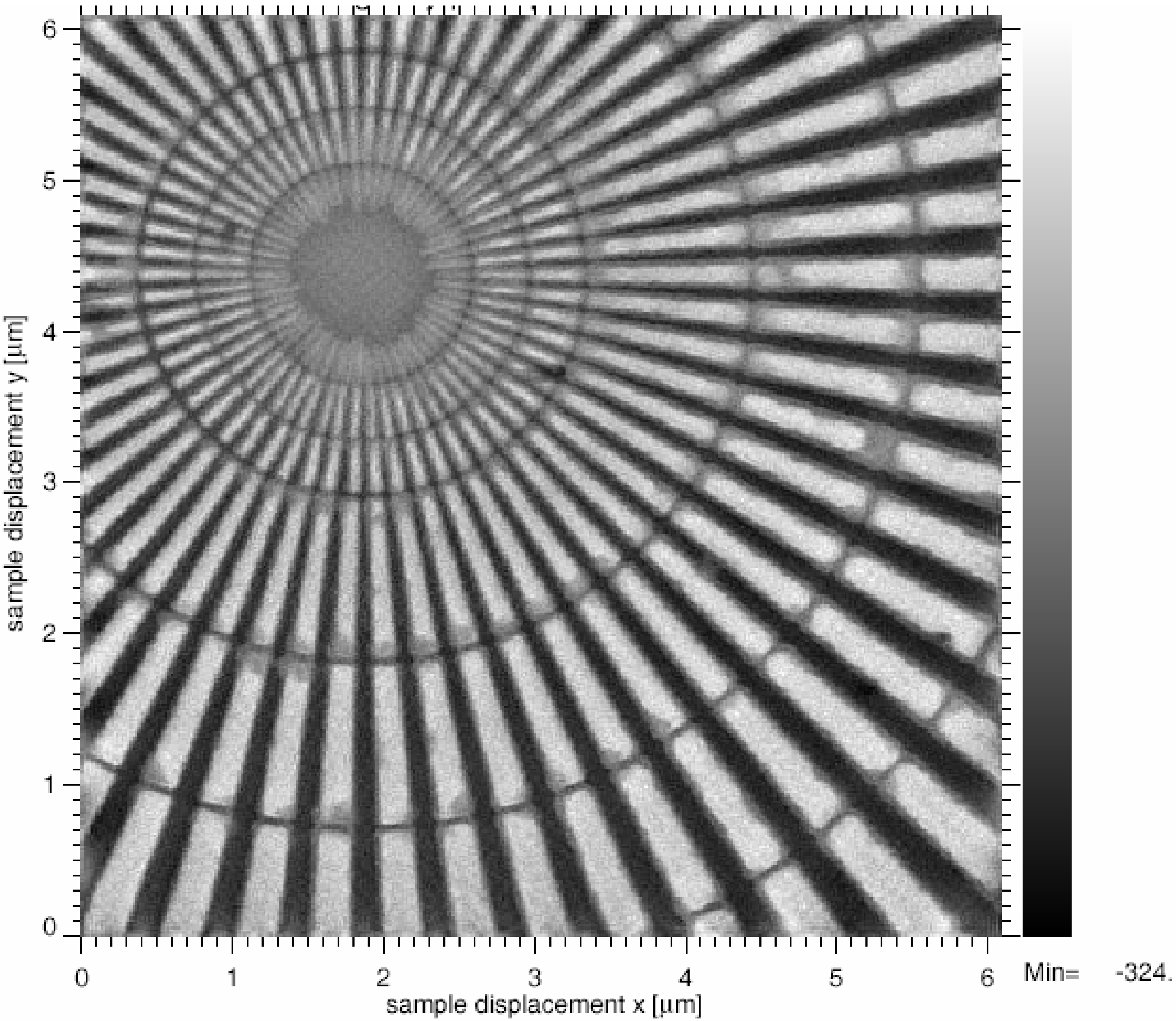
X-ray refractive index:
$n=1-\delta-i\beta$



All channels acquired simultaneously



Feser thesis



Feser thesis

- Bright field: easy to make quantitative
- Phase contrast: edge enhancement,
  good for high energy
- Dark field: emphasizes strong scatterers
- Luminescence: locates special labels
- Fluorescence: trace element sensitivity
  (high energy)

STXM developments
Stony Brook / NSLS

- Zone plates 1983-'85 IBM
  1987-'94: IBM/CXRO
  1995- Bell Labs/SB
- Many students, postdocs, over the years:
  - Ade, Buckley, Chapman, Feser, Jacobsen, Kaznacheyev, Kenney, Ko, Lindaas, Maser, McNulty, Miao, Neuhäusler, Osanna, Rarback, Schäfer, Spector, Vogt, Wang, Winn, Yang, Yun, Zhang…

Stony Brook group today:

- Faculty: Chris Jacobsen, Janos Kirz
- Students: Tobias Beetz, Holger Fleckenstein, Benjamin Hornberger, Myrna Lerotic, Enju Lima, Ming Lu, David Shapiro, Aaron Stein
- Guest scientist: David Sayre
- Beamline scientist: Sue Wirick

Agere Inc.: Don Tennant

Many collaborators…

Looking for postdoc!

SPEM vs XPEEM

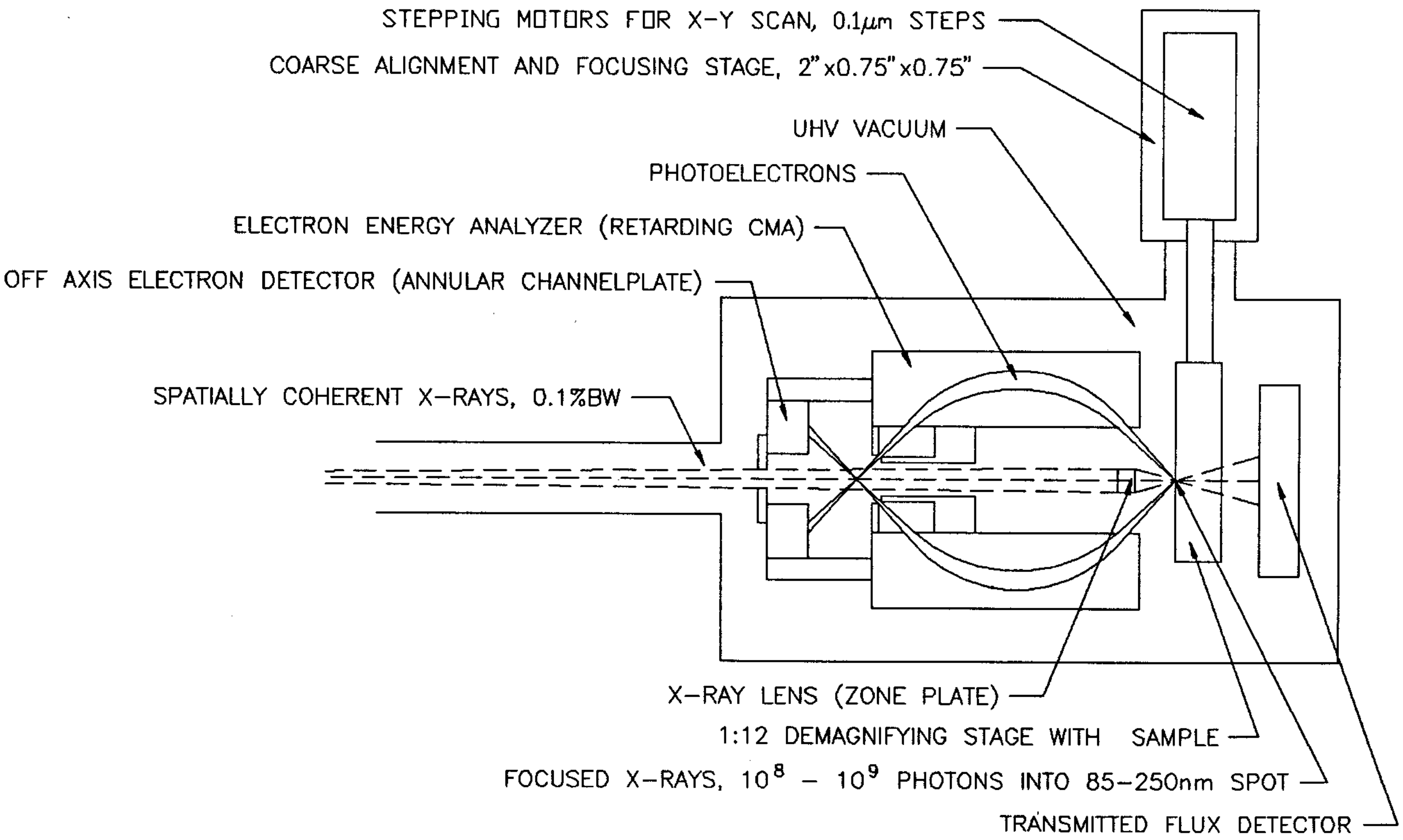
- SPEM
  - X-ray focus determines resolution
  - Photoelectrons, Auger
  - Chemical shift analysis
  - Point-spectra
- XPEEM
  - Full-field
  - Electron-optics determines resolution
  - Fast XANES using secondary electrons
  - New designs to correct aberrations

Charging of insulating specimens, radiation damage, and photon assisted deposition of organics can be of concern

SPEM history

- SPEM
  - H. Ade thesis
  - Zone plate (>250 eV)
  - CMA (we had one)
  - Design: XRM II, 280 ('88)
  - Demonstration: APL 56, 1841 ('90)
  - Follow-up:
    - Ko thesis (HSA) – died
    - ALS - died
    - ELETTRA
    - NSRRC
    - Pohang
- MAXIMUM
  - Cerrina, Underwood et al.
  - Schwarzschild mirror (<120 eV)
  - CMA
  - Design: NIM A266, 303 '88
  - Demonstration: SPIE 1741, 296 ('93)
  - Follow-up:
    - MAXIMUM @ ALS – died
    - SUPER-MAXIMUM @ ELETTRA

Original Stony Brook SPEM @ NSLS



Ade et al. 1990 APL

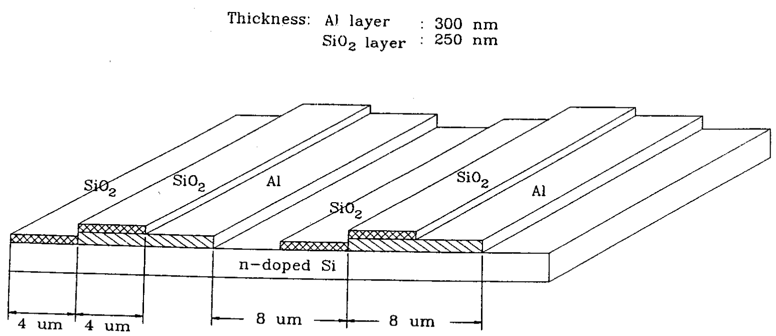
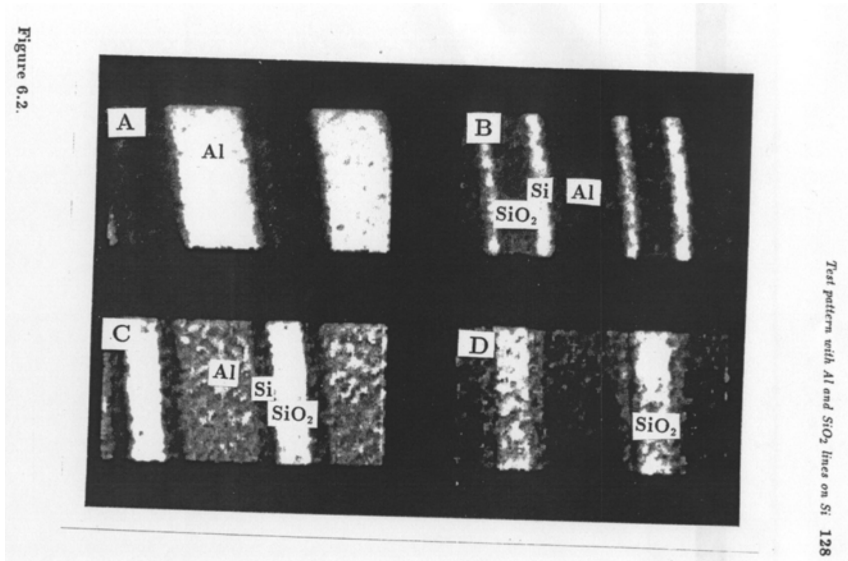


Figure 7. Schematic of the test pattern utilized to demonstrate parallel imaging for chemical state mapping.



H. Ade & C.-H. Ko 1995

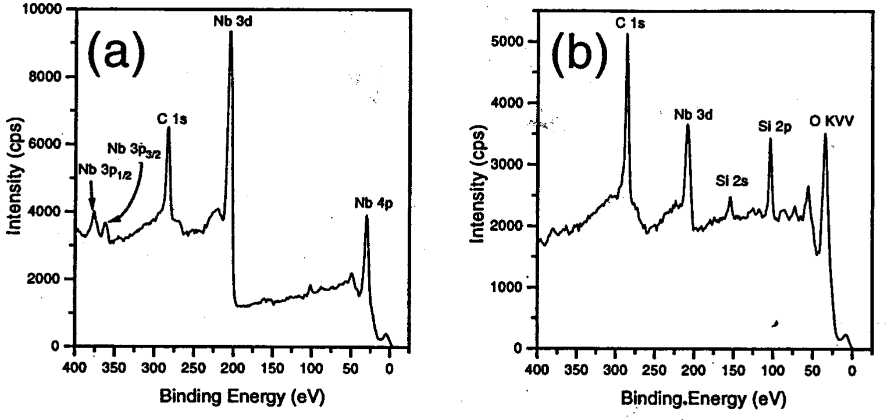


Figure 6. (a) spectrum from area outside the hole, (b) spectrum from inside one of the 3 μm diameter holes. The most prominent photoelectron and Auger peaks are identified and labeled. Note, that the O KVV Auger and the Nb 4p are overlapping, but are at slightly different energies. (Photon energy was 540 eV). The acquisition time for each spectrum was a few min (400 msec dwell time per 1 eV data point) and corresponds to a probe about 250 nm FWHM in size.

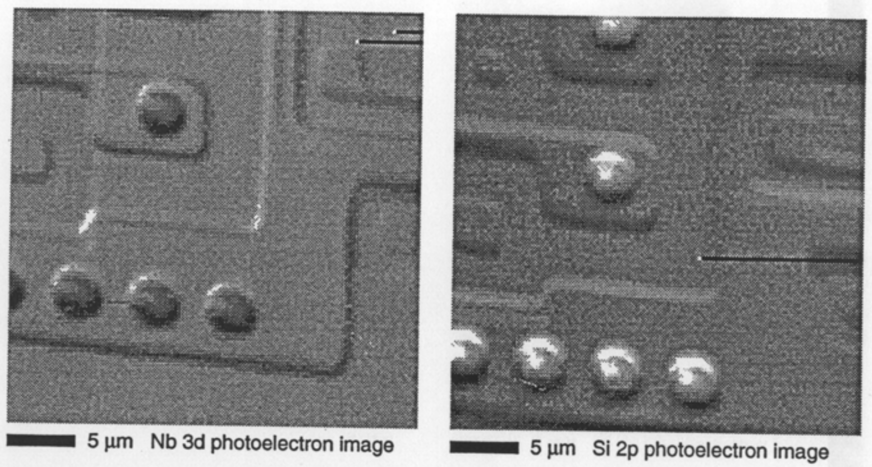
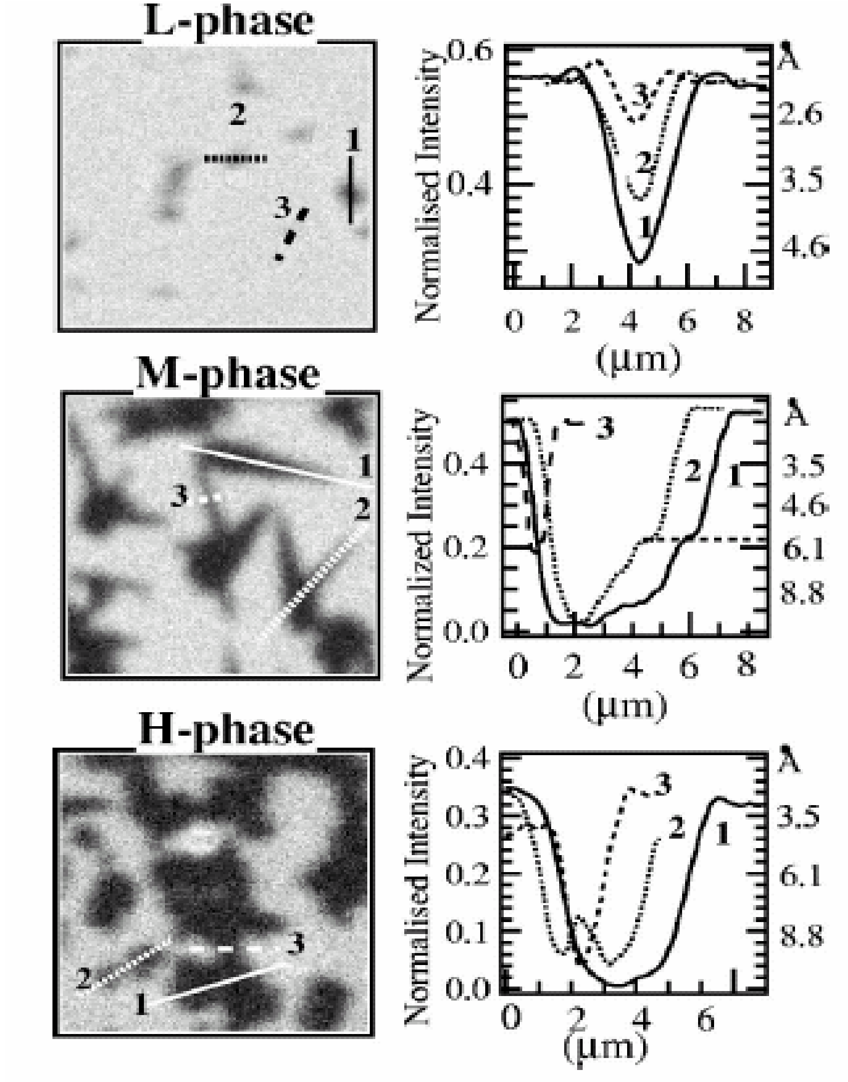


Figure 5 a) 'Summed' photoelectron image utilizing the Nb 4p photoelectrons, b) 'summed' photoelectron image of about the same area as in Fig 5a with the HSA tuned to the Si 2p photopeak. (Same scan parameters as in Fig. 4.)

SPEM today

- Hemispherical analyzer
- Multichannel detector
- Sub-micron resolution
- A. Böttcher et al., J. Chem. Phys. 117, 8104 (2002)
- Oxide growth on Ru(0001)



Lensless Imaging

David Sayre, Chris Jacobsen,
David Shapiro, Tobias Beetz, Enju Lima

Stony Brook University

Malcolm Howells
Lawrence Berkeley National Laboratory

Why go lensless?

- A technique for 3D imaging of 0.5 – 20 μm isolated objects
- Too thick for EM (0.5 μm is practical upper limit)
- Too thick for tomographic X-ray microscopy (depth of focus < 1 μm at 10 nm resolution for soft X-rays even if lenses become available)

Goals

- 10 nm resolution (3D) in 1 - 10μm size biological specimens

  (small frozen hydrated cell, organelle; see macromolecular aggregates)

  Limitation: radiation damage!

- <4 nm resolution in less sensitive nanostructures

  (Inclusions, porosity, clusters, composite nanostructures, aerosols…)

  eg: molecular sieves, catalysts, crack propagation

Image reconstruction from the diffraction pattern

- Lenses do it, mirrors do it
  - but they use the full complex amplitude!
- Recording the diffraction *intensity* leads to the "phase problem"!

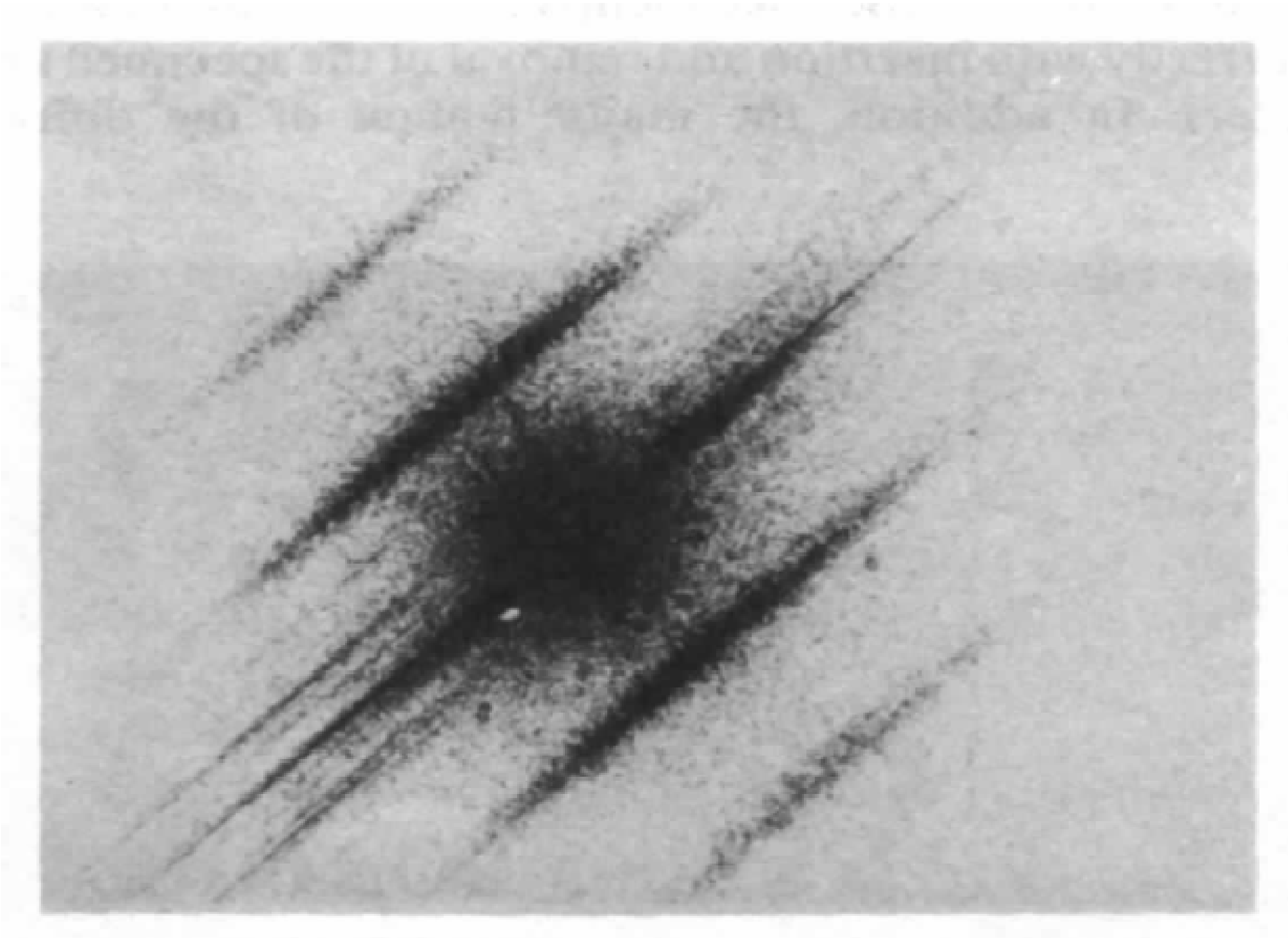
- Holographers do it – but they mix in a reference wave, need very high resolution detector or similar precision apparatus

- Crystallographers do it – but they use MAD, isomorphous replacement, or other tricks (plus the amplification of many repeats)

History

- Sayre 1952: Shannon sampling theorem in crystallography
- Gerchberg & Saxton, 1971: iterative phase retrieval algorithm in EM
- Sayre 1980: pattern stronger with soft X-rays; use SR to work without xtals!
- Fienup 1982: Hybrid Input-Output, support
- Bates 1982: 2x Bragg sampling gives unique answer for ≥ 2 dimensions
- Yun, Kirz &Sayre 1984-87: first experimental attempts

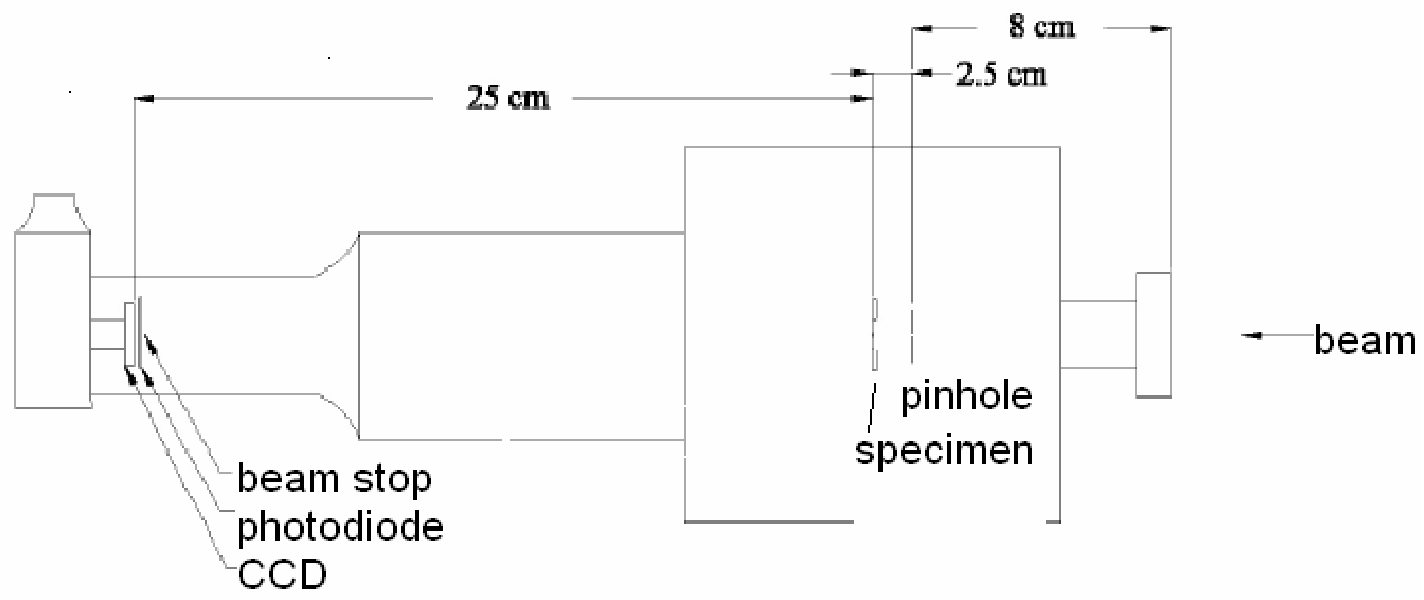
Diffraction pattern of a single diatom, 1987



Yun, Kirz & Sayre, Acta A.

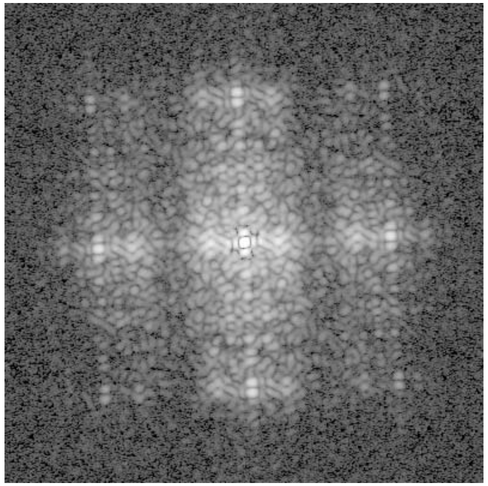
Modern era

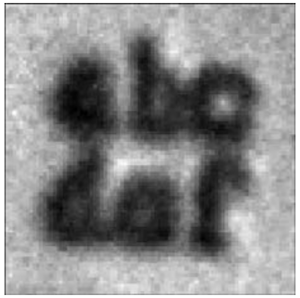
- 1998: Sayre, Chapman, Miao: oversampling & Fienup algorithm for X-rays
- 1999: first experimental demonstration in 2D



Miao, Charalambous, Kirz, Sayre, *Nature* **400**, 342 (1999).

λ=1.8 nm soft x-ray diffractio n pattern





Low angle data From optical micrograph

Scanning electron micrograph of object

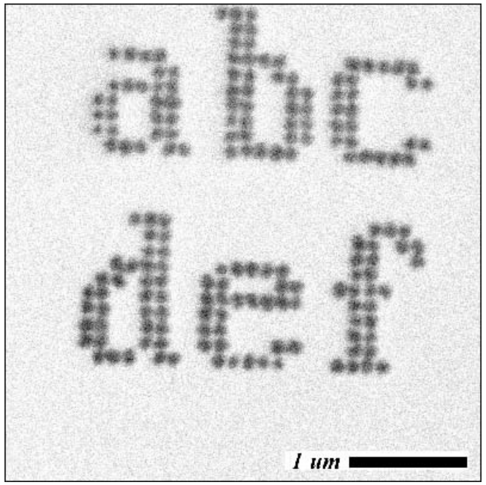


Image reconstructed from diffraction pattern (θ_{max} corresponds to 80 nm). Assumed positivity

Basic principles

- Single object, plane wave incident, scattered amplitude is Fourier transform of (complex) electron density $f(\mathbf{r})$

$$F(\mathbf{k}) = \int f(\mathbf{r})\, e^{-2\pi i\, \mathbf{k} \cdot \mathbf{r}}\, d\mathbf{r}$$

- Assume: Born Approximation
- Assume coherent illumination:

for object size a, resolution d,

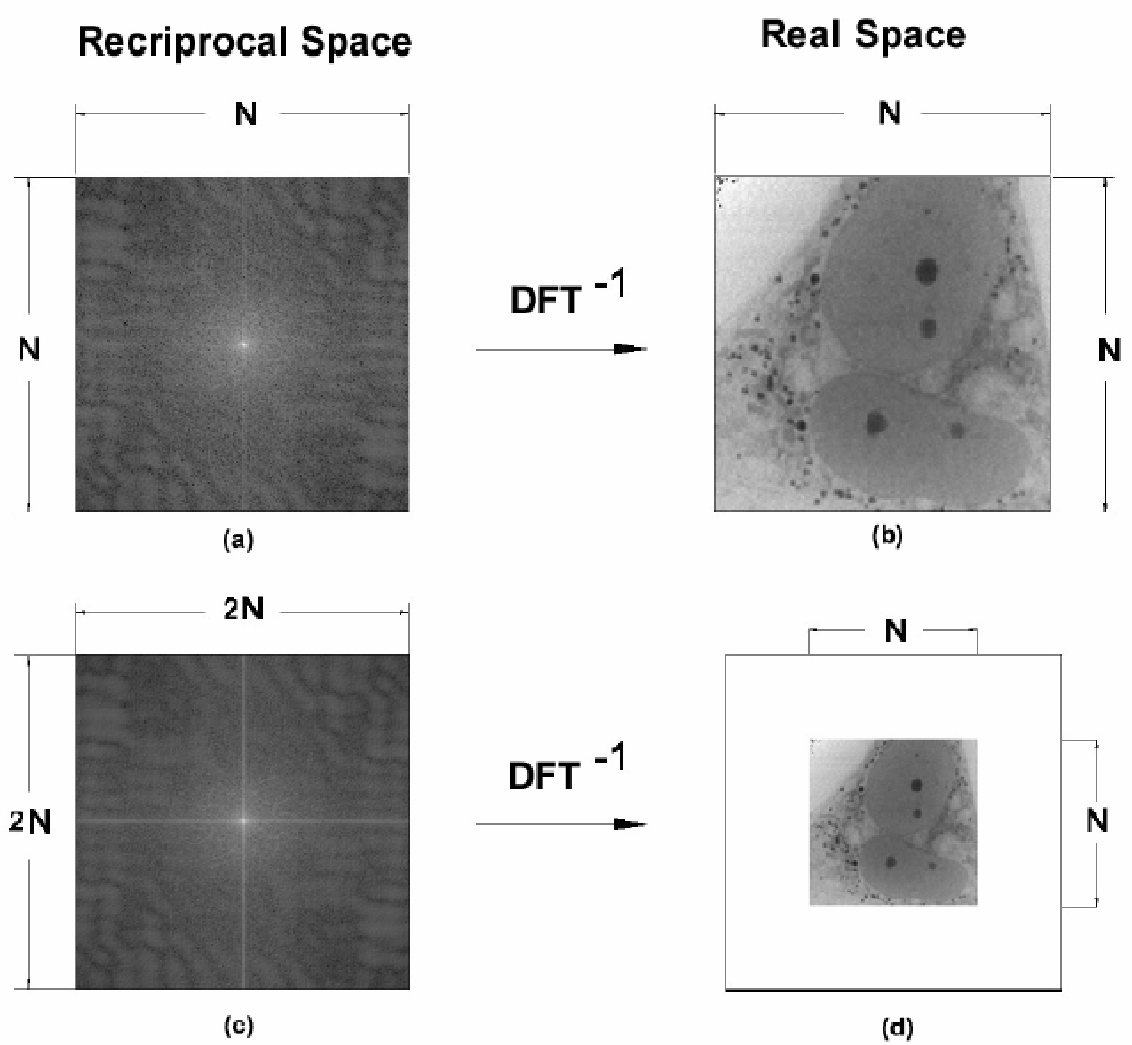
  - spatial coherence $\delta\theta < \lambda/4a$
  - temporal coherence $\delta\lambda/\lambda < d/4a$

“Oversampling”:

Non-crystals:
pattern continuous,
can do finer sampling
of intensity

Finer sampling;
larger array;
smaller transform;
“finite support”

(area around specimen
must be clear!)

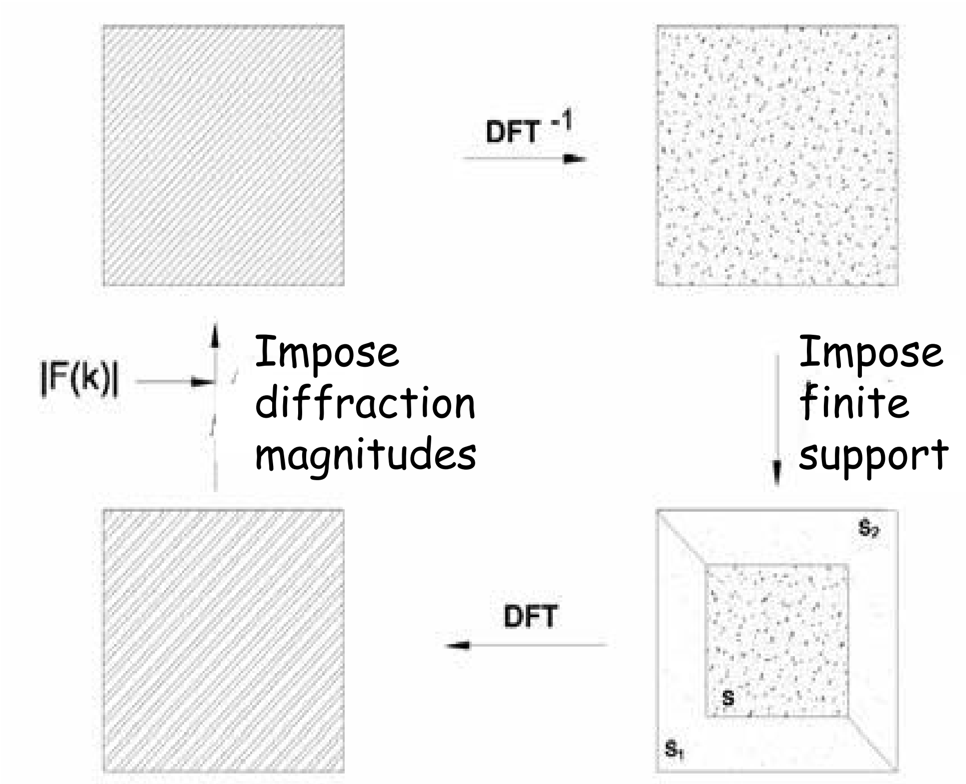


Reconstruction

Equations can still not be solved analytically

Fienup iterative algorithm

Reciprocal space Real space



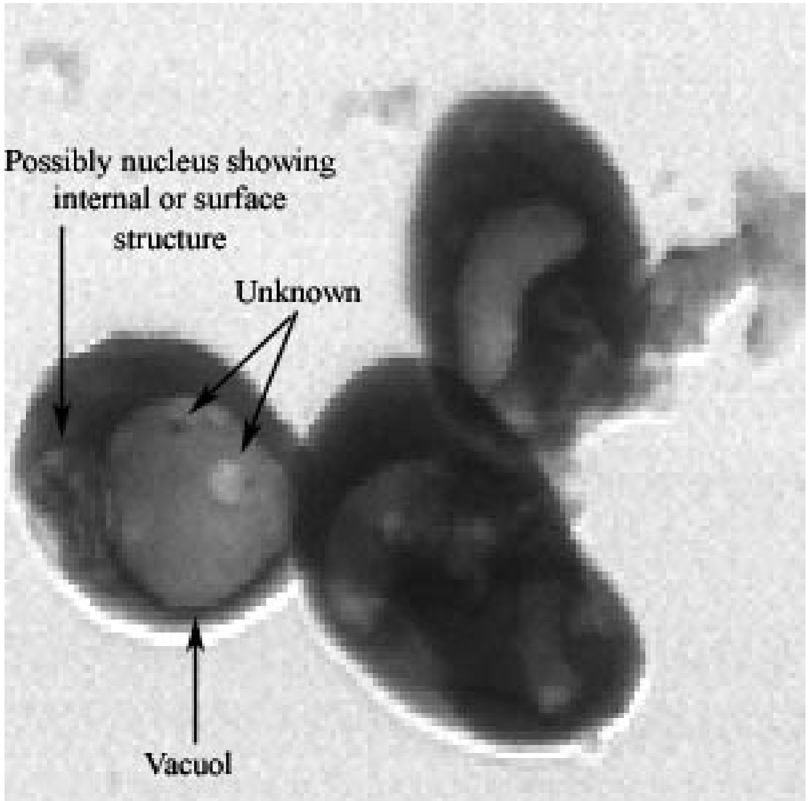
•Positivity of electron density helps!

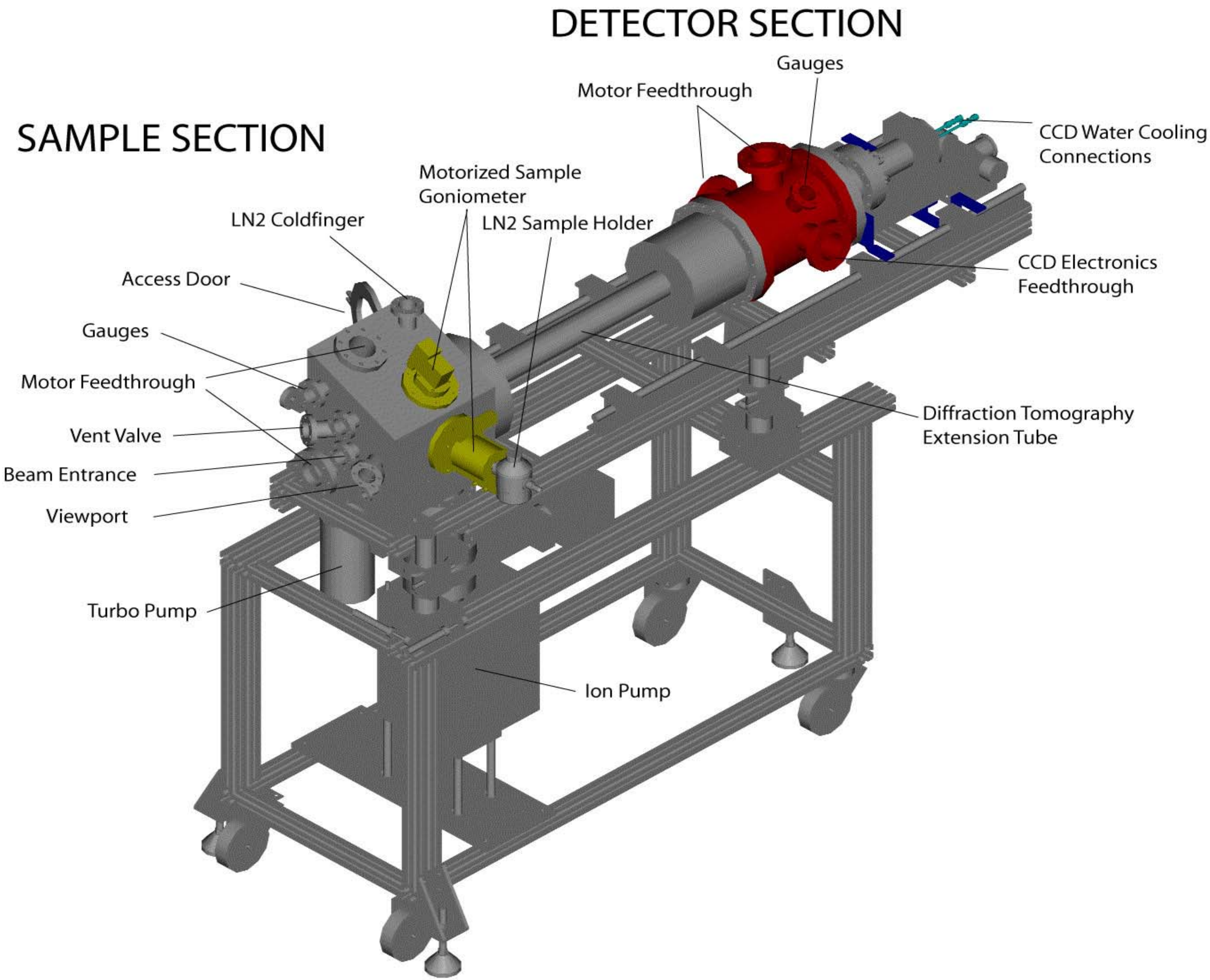
Recent Successes

- Miao et al. (Stanford/Spring 8)
  - -First biological specimens (PNAS 100, 110, 2003)
  - -First 3D reconstruction (PRL 89, 88303, 2002)
- Howells, Spence, Chapman et al (ASU, LBL, LLNL)
  - –Reconstruction without low resolution image (Acta A59, 143 2003)
- Robinson et al. (Illinois)
  - -reconstruction of nano-crystal from structure of Bragg peak (PRL 87, 195505, 2001)

Near-term future

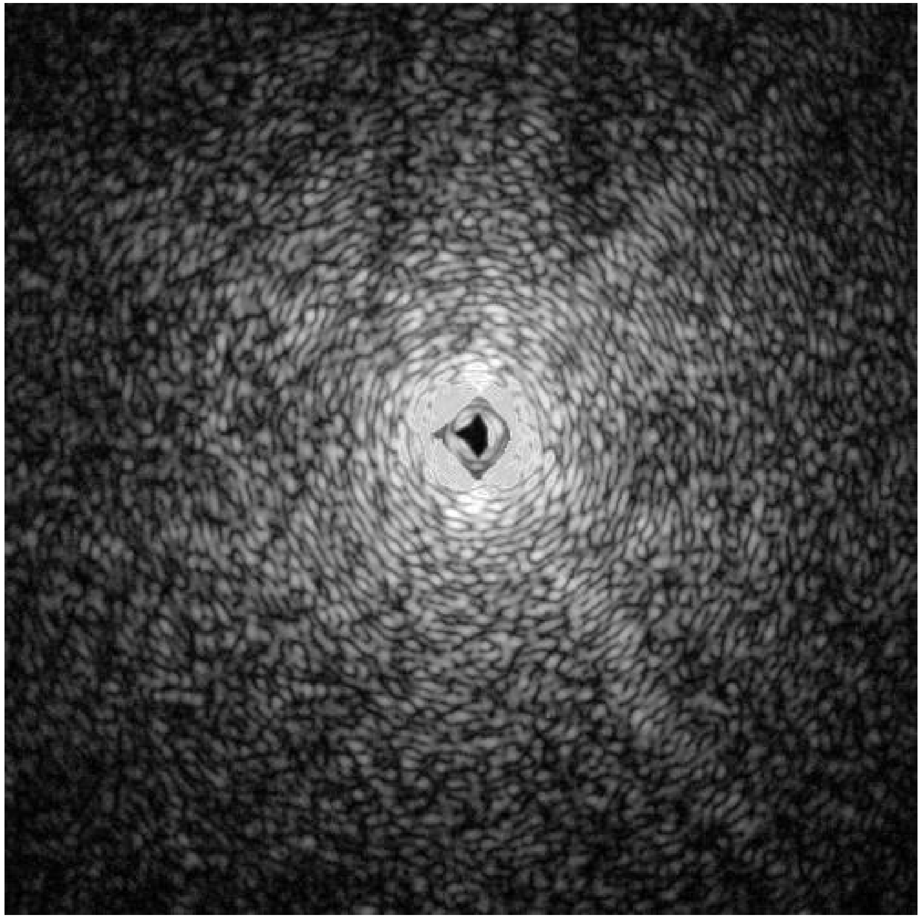
- Stony Brook/NSLS chamber
  - Incorporates low resolution X-ray microscope
  - Provision for frozen hydrated samples
  - Precision positioning and rotation of specimen, optics
- Our Goals:
  - Develop technique (recording and reconstruction)
  - Study dose vs resolution; damage limits
  - 3D reconstruction of frozen hydrated dwarf yeast cell

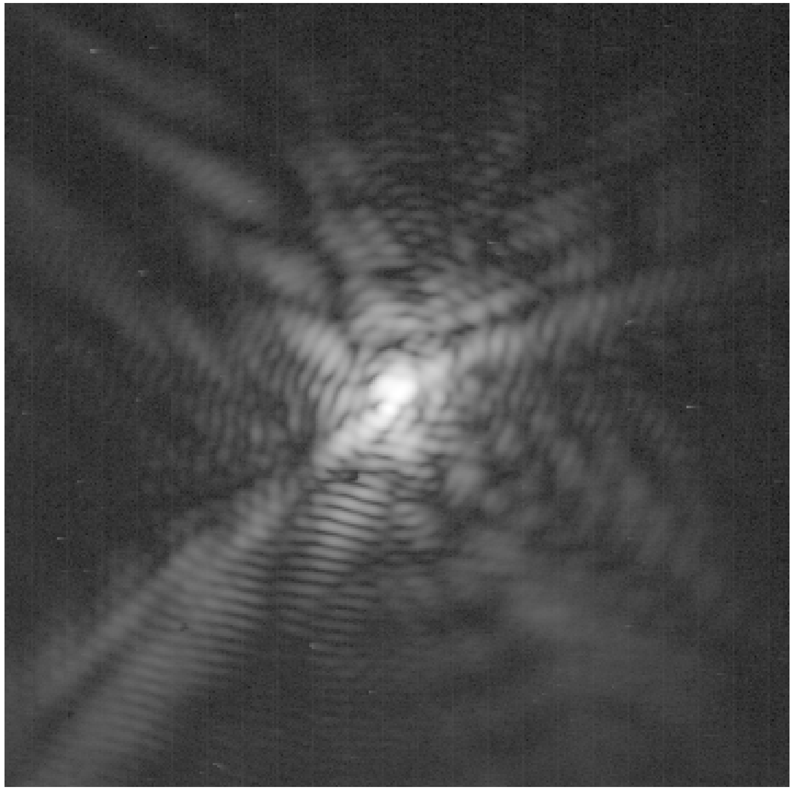




DETECTOR SECTION
SAMPLE SECTION
Gauges
Motor Feedthrough
CCD Water Cooling Connections
Motorized Sample Goniometer
LN2 Coldfinger
LN2 Sample Holder
CCD Electronics Feedthrough
Access Door
Gauges
Motor Feedthrough
Diffraction Tomography Extension Tube
Vent Valve
Beam Entrance
Viewport
Turbo Pump
Ion Pump

New apparatus: Diffraction patterns from yeast cells





Where we really want to be

- Collect a high resolution 3D data set in an hour or two
- Reconstruct reliably in a comparable amount of time