Synchrotron X-ray Tomography of Flame Retardants in Polymers

Kyungmin Ham[1], Heath A. Barnett[2], and Les Butler[2]

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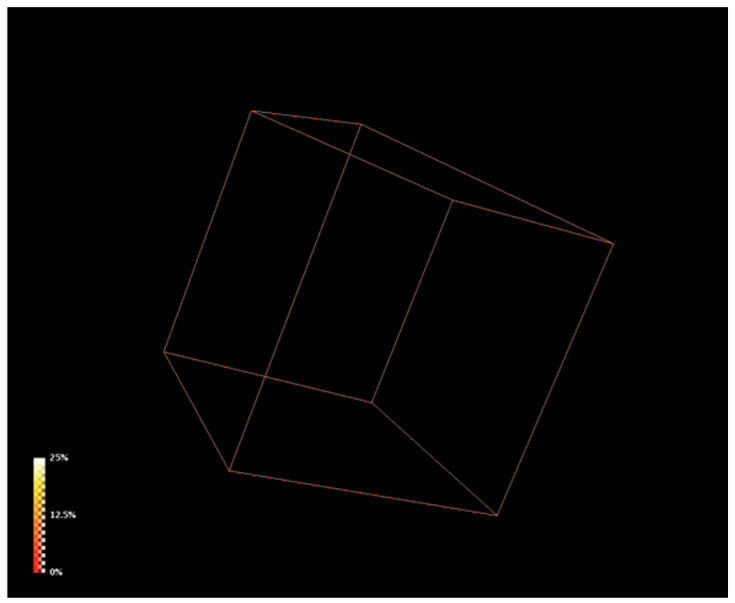
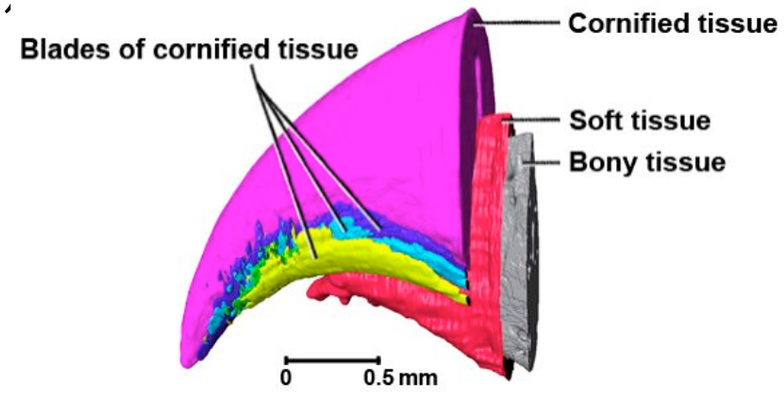


- tomography: X-ray (and e- and neutron)
  - resolution: micron to nanometers
  - time: minutes to hours
  - chemistry: elemental and phase
- flame retardants in polymer blends
  - snapshot of an inhomogeneous distribution
  - radial distribution about fiber reinforcement
  - diffusion as a function of annealing
- needed: instrumentation, mathematics, software

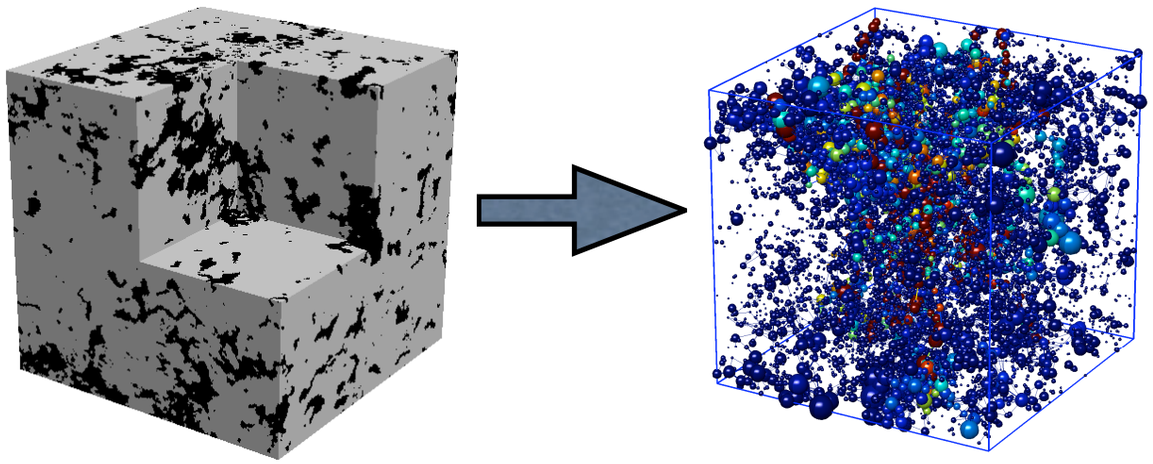
software stack (Ed)

- 10 GB per experiment (1 - 10 expts/day)
- LLNL VisIT (parallelized visualization)
- file types: HDF5 and DICOM
- huge metadate needs
  - currently: FileMaker Pro and collaborators append metadate to links to HDF5 files
- collaborators in LaTech, APS, Munich, and industry

New structures in cat claws discovered with synchrotron X-ray tomography.
Homberger, 2007



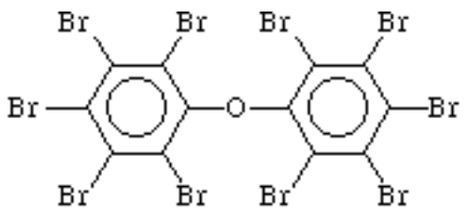
Real sandstone samples provides authentic geometry for flow modeling. Applications range from environmental remediation to oil&gas recovery.
Thompson & Willson, 2008



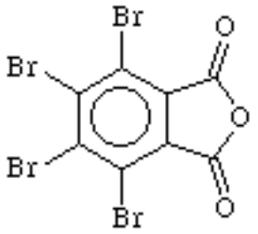
flow rates
red = fast
blue = slow

Tomography and chemistry: Dispersion of flame retardants in polystyrene

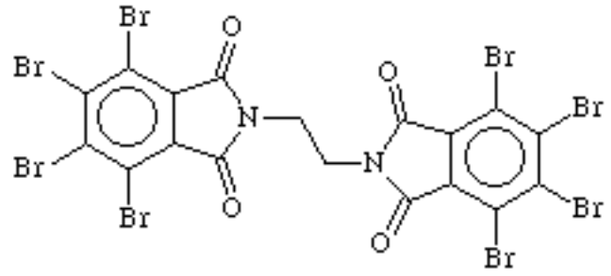
- BT-93, a phthalimide dimer, and antimony(iii) oxide as synergist.
- CRT case can be up to 20 wt% Br.
- How well mixed at the micrometer scale?
- Are the chemical distributions correlated?
- As a function of time, does the system exhibit Ostwald ripening and “blooming”?



1-(2,3,4,5,6-pentabromophenoxy)-2,3,4,5,6-pentabromobenzene (Saytex 102)



3,4,5,6-tetrabromophthalic anhydride (Saytex RB-49)



3,3',4,4',5,5',6,6'-octabromo-*N*,*N*'-ethylenediphthalimide (Saytex BT-93)

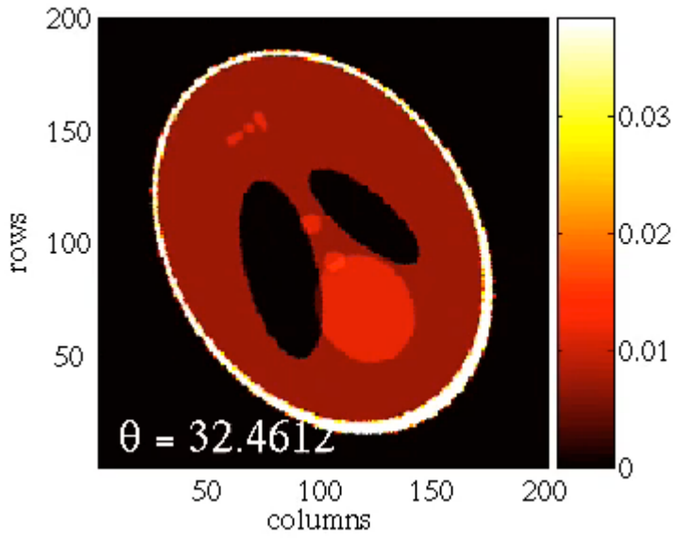
Some 3D Methods for Chemical Imaging

Technique	Resolution, Field of View, Expt. Time	Comments
synch. X–ray	2 μm, 1024^3, 1-8 hrs	> 10 beamlines in US, mature, reliable, great elemental sensitivity for $Z \geq 35$ (Br)
^{13}C & ^{31}P MRI	400 μm, 128^3, 6 hrs	lowest S/N, poorest resolution, best chemical speciation
neutron tomo.	50 μm, 1024^3, 2 hrs	~6 beamlines worldwide, some in renovation, elemental sensitivity. US: NIST, UC Davis
electron micro. tomo	2 nm, 512^3, ? hrs	in development; best sample geometry is a thin rod
microtome & 2D EM	2 x 2 x 50 nm, $>1024^3$, >12 hrs	labor intensive; problems with slice-to-slice alignment

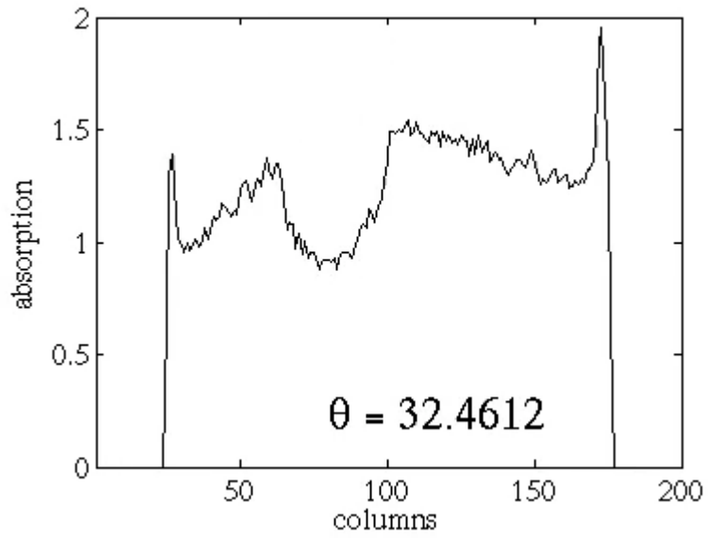
Tomography with “Golden ratio” ordering

X-rays

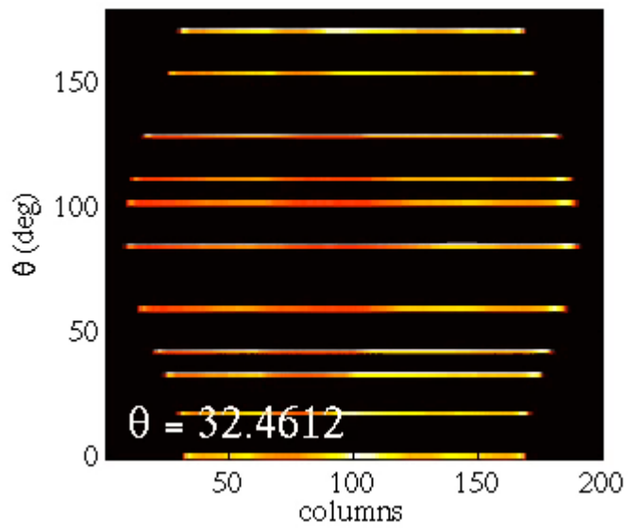
rotate sample



acquire projections



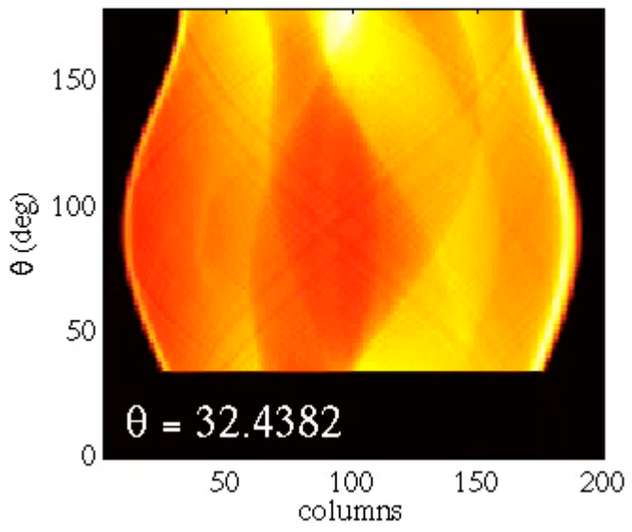
store projections in “sinogram”



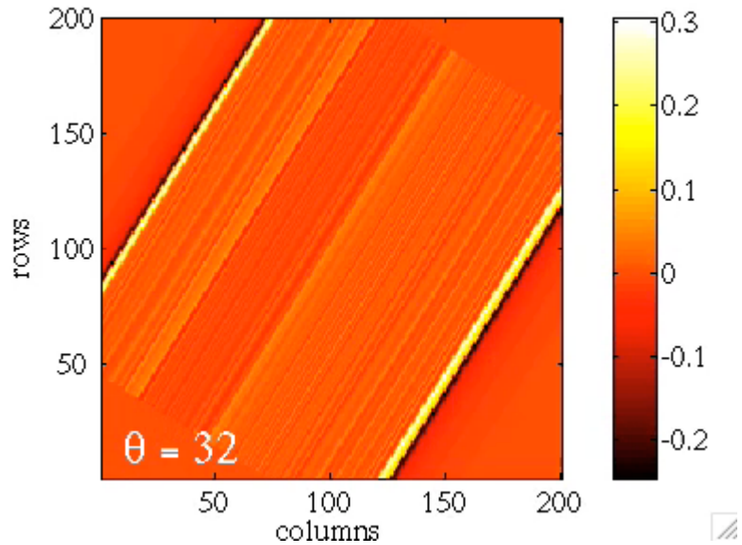
With GR, we can terminate experiment early, if necessary, and still have a reasonable image reconstruction.

Backprojection reconstruction

use each projection

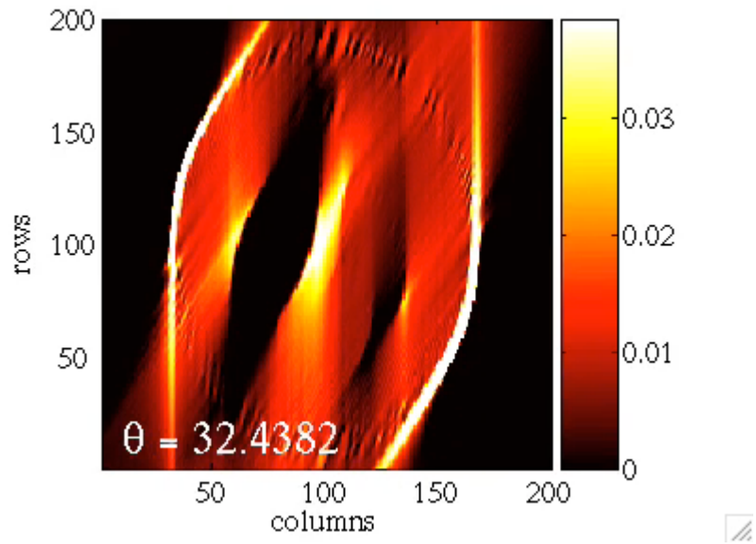


filter and rotate projections

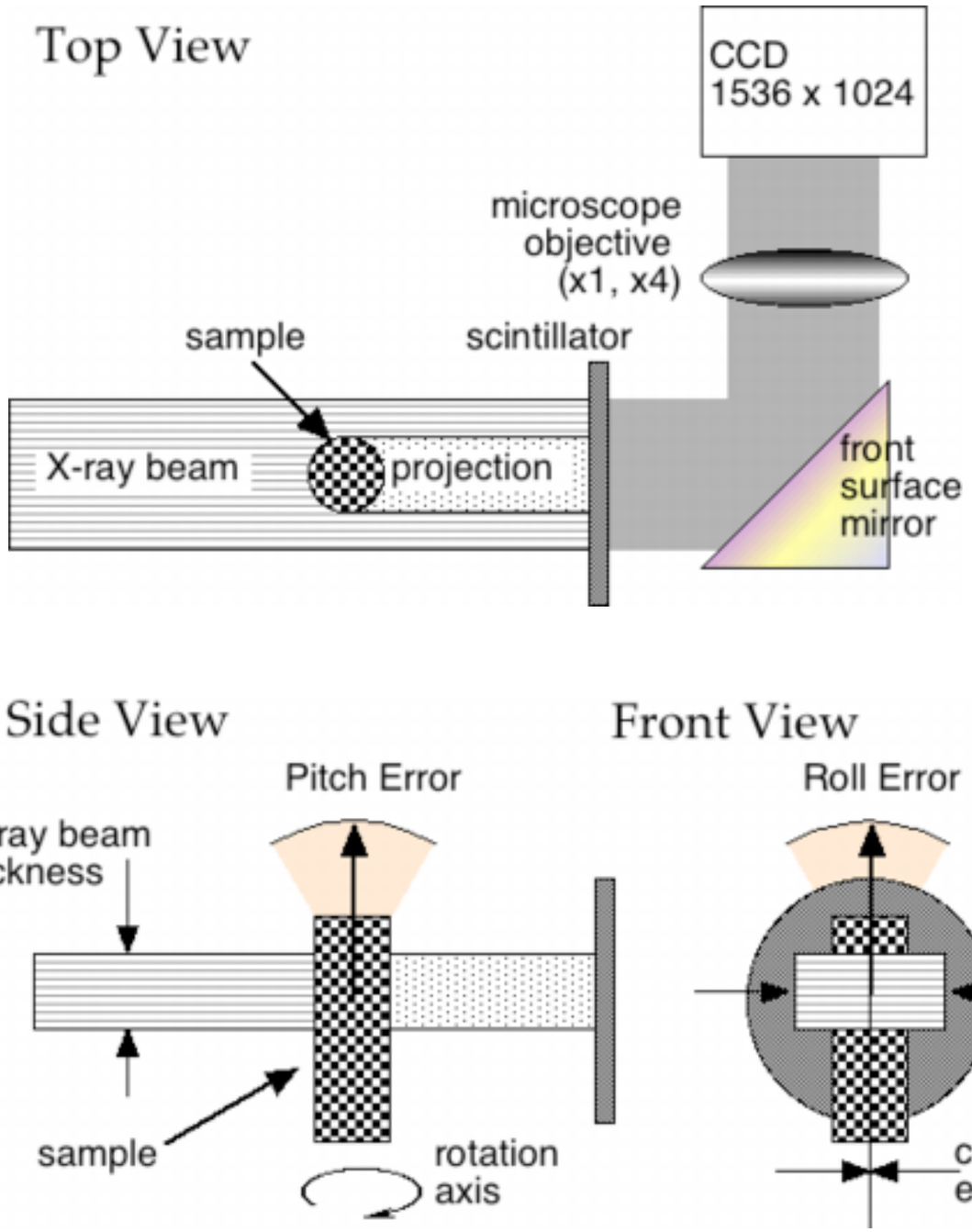


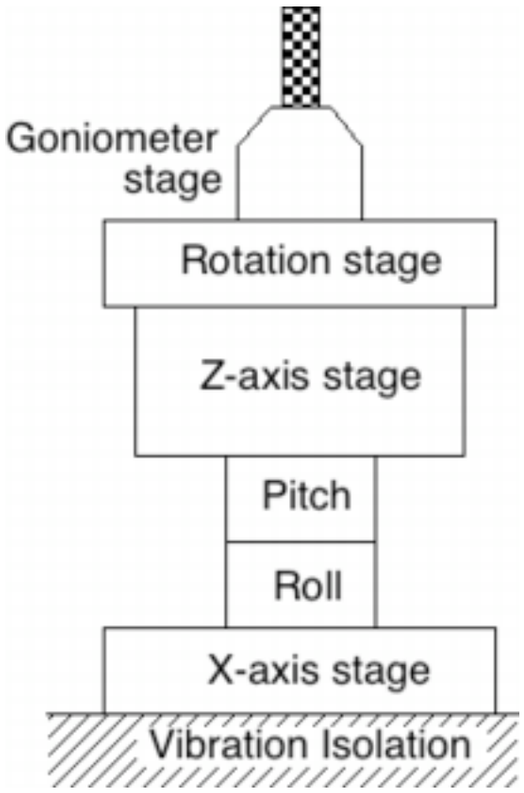
Back-projection reconstruction

sum all projections to reconstruct image



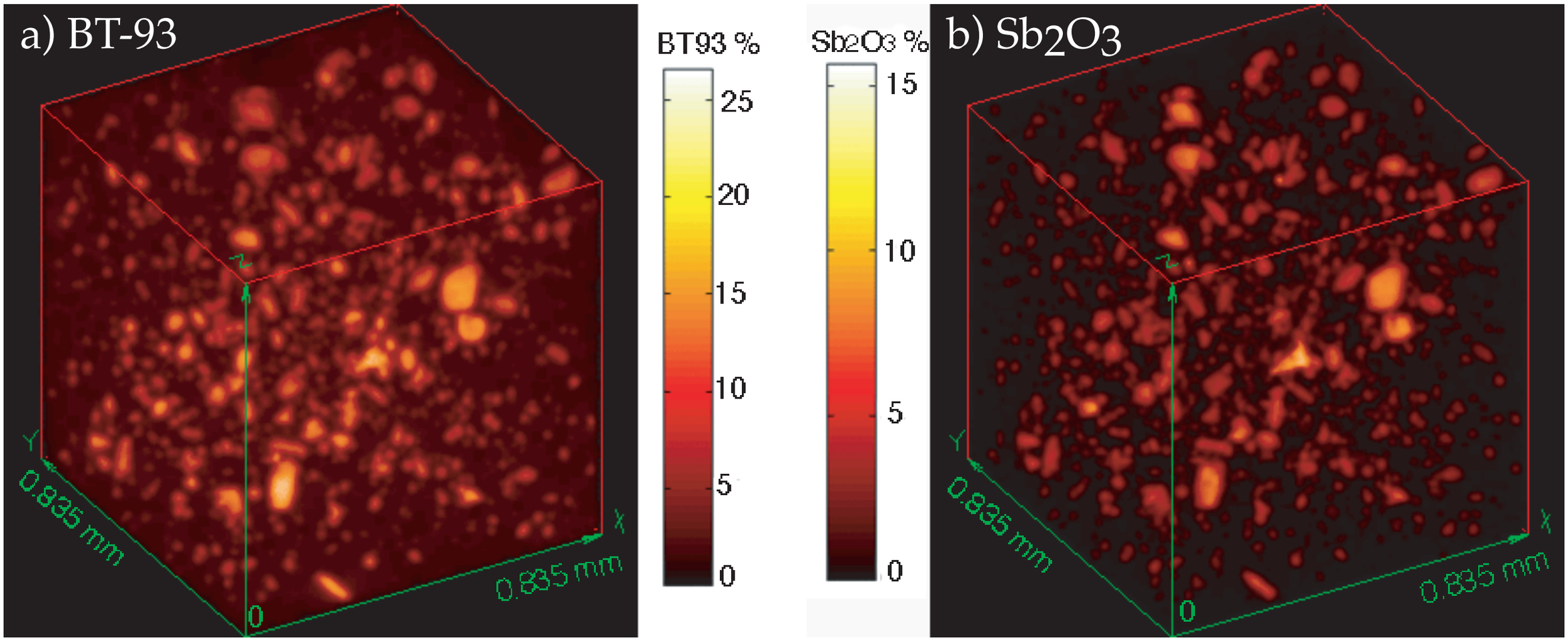
Tomography: Acquire transmission views as a function of sample rotation angle. Requires high-accuracy sample motion, high-resolution scintillator/CCD.





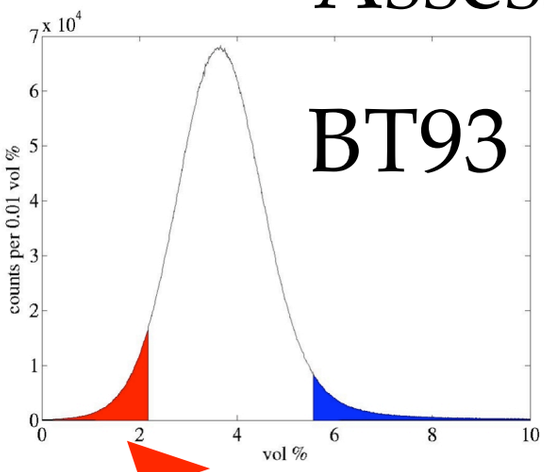
Kyungmin Ham, Hua Jin, Leslie G. Butler, and Richard L. Kurtz, *Rev. Sci. Instr.*, **2002**, *73*, 1521-3

- Least squares fit of X-ray images yields two volumes of data showing BT-93 and Sb_2O_3 concentration distributions. The colorbars show volume percent composition.
- Spatial correlation is obvious. Correlated with mixing order.

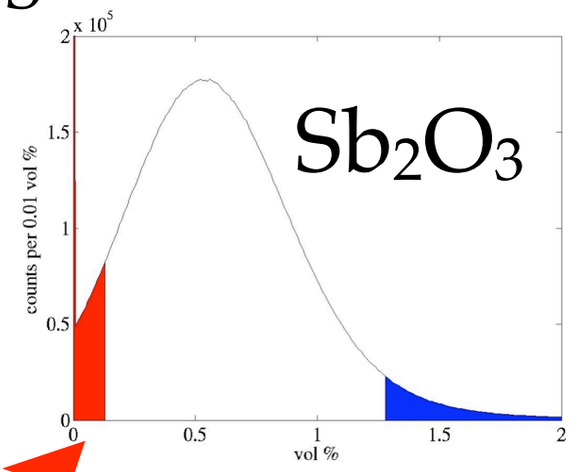


Ham, K.; Jin, H.; Al-Raoush, R.; Xie, X.; Willson, C. S.; Byerly, G. R.; Simeral, L. S.; Rivers, M. L.; Kurtz, R. L.; Butler, L. G. *Chemistry of Materials*, 2004, *16*, 4032-42.

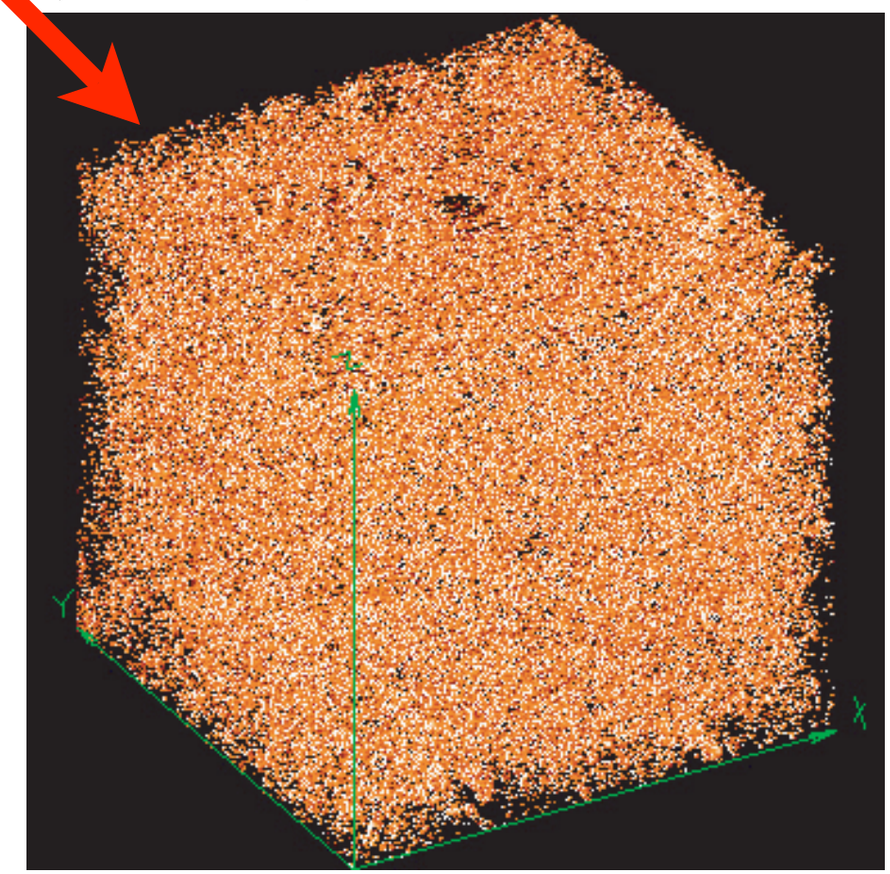
Assessments of dispersions: the extremes



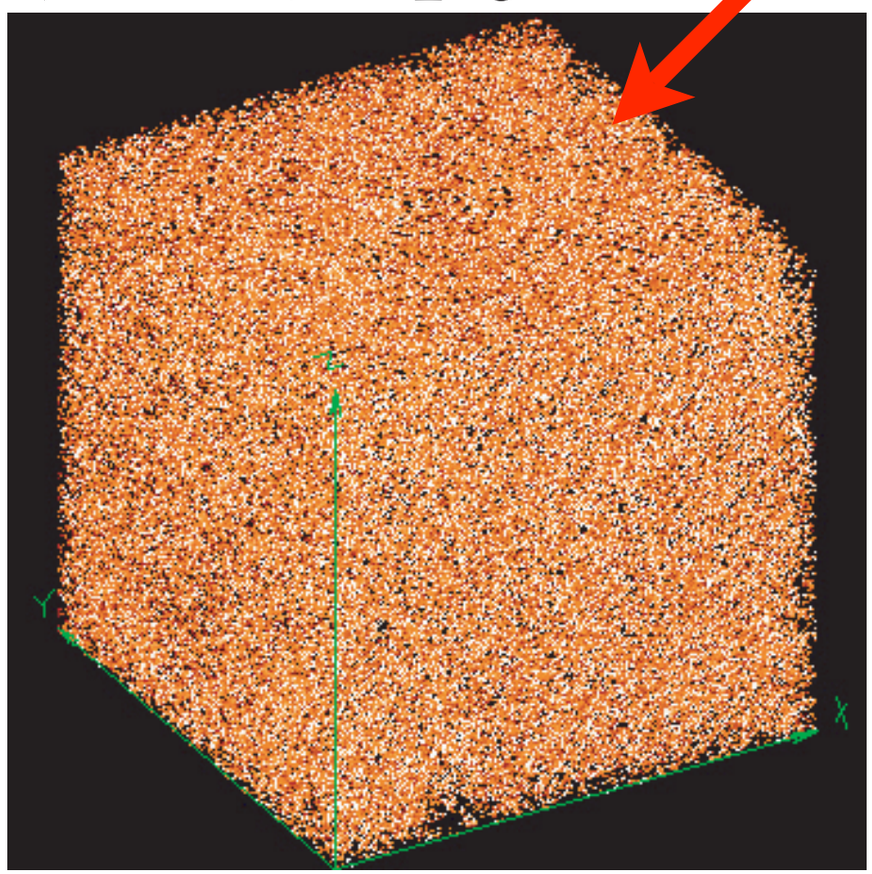
Safety



a) <2.2 vol% BT-93



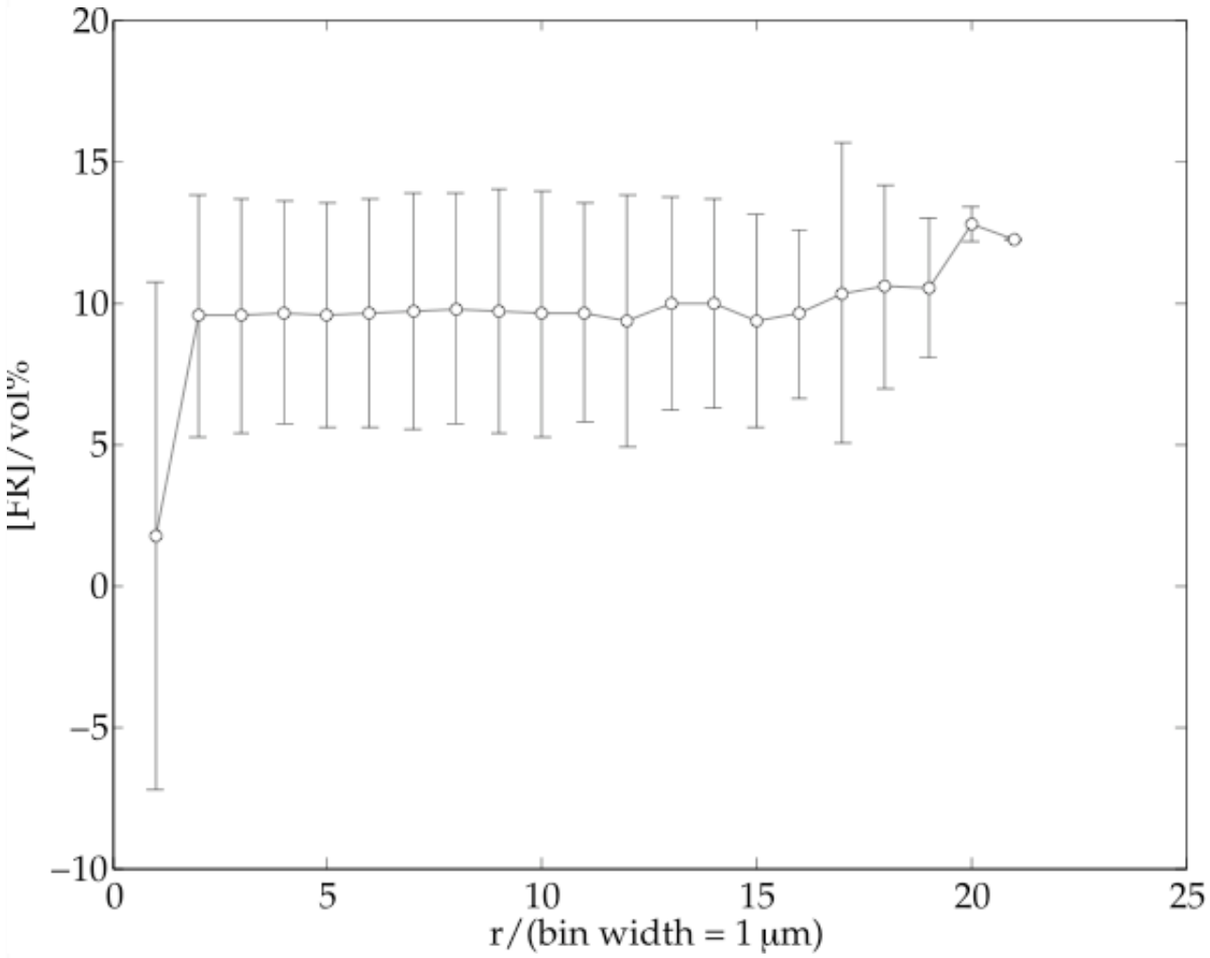
b) <0.1 vol% Sb_2O_3



By inspection, there appear to be no large, connected regions in red, that is, no regions large enough to support a flame. Thus, the mixing is judged to be good enough to make a safe material.

Sample: Fiberglass reinforced nylon with flame retardant and Sb_2O_3

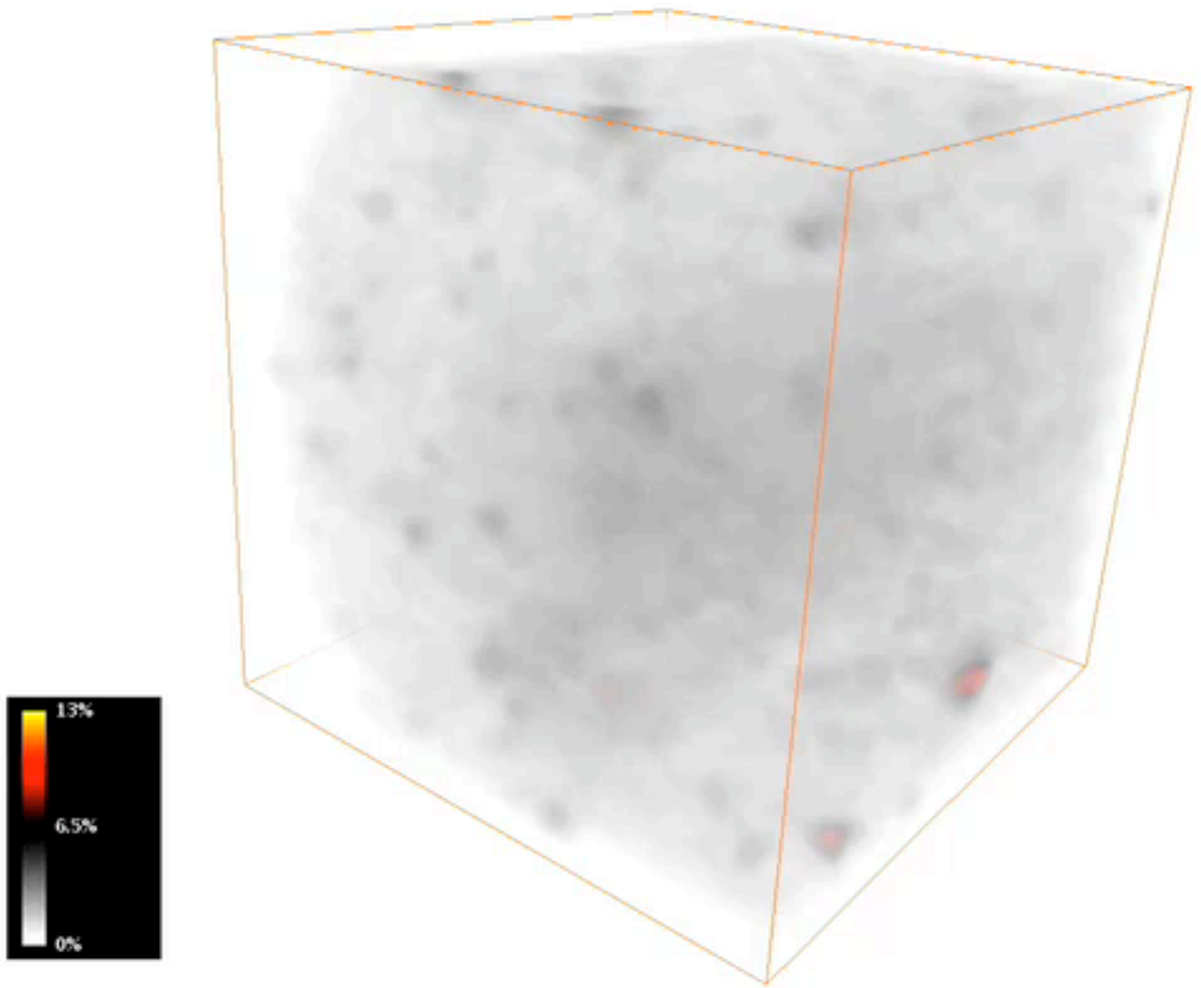
Questions: What are FR and Sb_2O_3 concentrations around fibers?

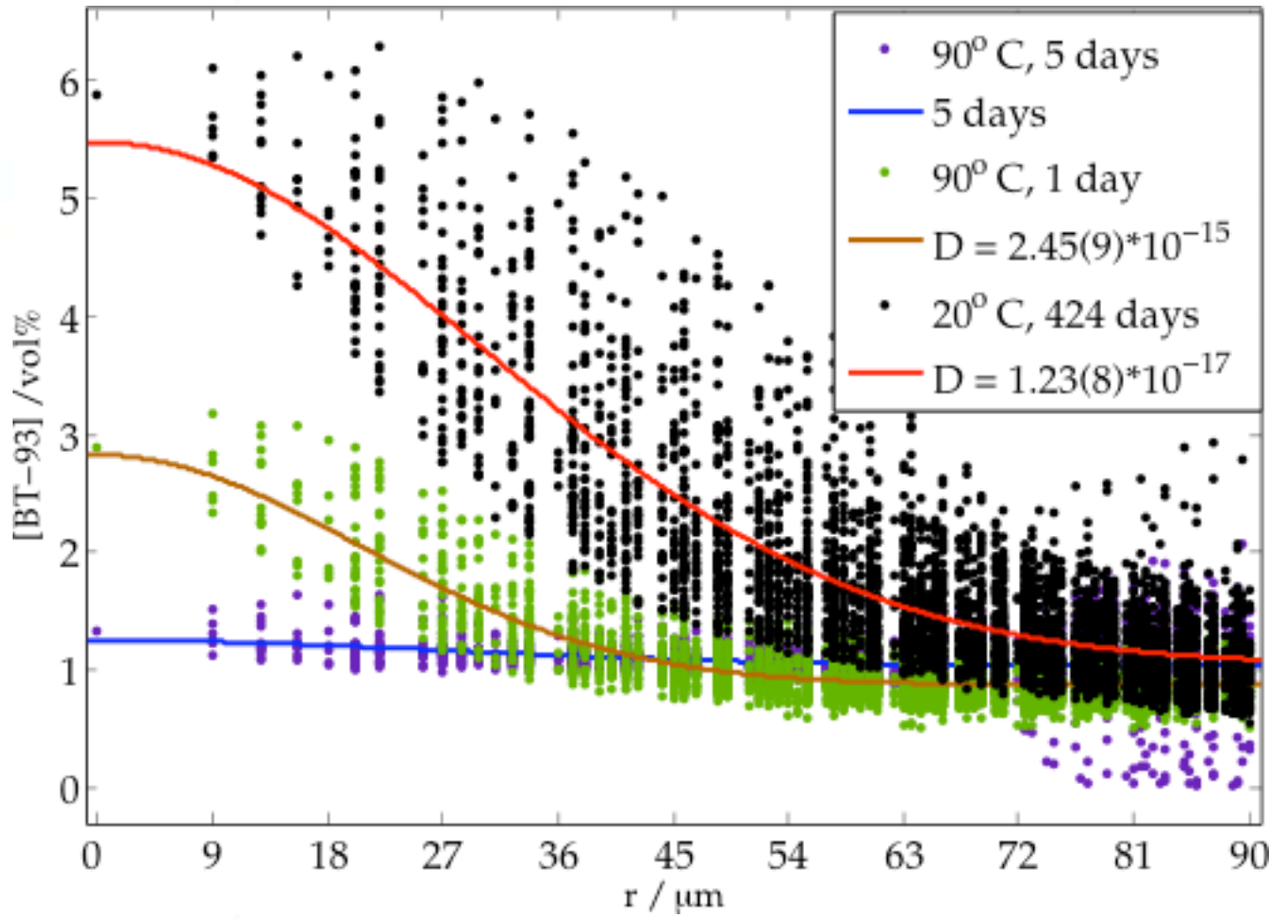


Barnett, H. A.; Ham, K.; Scorsone, J. T.; Butler, L. G. *Journal of Physical Chemistry B*, submitted

Sample: Flame retardant with inital poor blend.

Question: Can dissolution of FR as a function of anneal time/ temperature be measured?





Barnett, H. A.; Ham, K.; Butler, L. G., *Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms*, 2007, in press.

Mathematics: Need more reconstruction and 3D image analysis

Jan 9-12, 2006 in Minnesota
http://www.ima.umn.edu

IMA - Institute for Mathematics and its Applications

Imaging, September 2005-June 2006

IMA Workshop:

3-D Image Acquisition and Analysis Algorithms

January 9-12, 2006

Organizers:

Les Butler
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Louisiana State University
lbutler@lsu.edu
http://chemistry.lsu.edu/butler/

Gestur Olafsson
Department of Mathematics
Louisiana State University
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Todd Quinto
Department of Mathematics
Tufts University
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Program Solicitation
Calendar
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Schedule	Participants	Registration	Feedback
Dining Guide			Maps

Schedule and list of participants are not yet available.

New mathematics and algorithms are needed for 3-D image acquisition and analysis. The 3-D images come from many disciplines: biomedicine, geology, chemistry, and microfabrication. The mathematics is wide-ranging and includes at least tomography and inverse problems, wavelets, PDE, and conformal mapping. The depth of the problem and the extent of the mathematics argues for multiple, long-duration collaborations that are fostered by a workshop series.

IMA theme for Sept ’08 - June ’09
“Mathematics & Chemistry”

Instrumentation: How to image phosphorus-based flame retardants?

Technique	Resolution, Field of View, Expt. Time	Comments
Synch. X–ray	2 μm, 1024^3, 1-8 hrs **new: 30 nm!!**	> 10 beamlines in US, mature, reliable, great elemental sensitivity for Z ≥ 35 (Br)
^{13}C & ^{31}P MRI	400 μm, 128^3, 6 hrs	lowest S/N, poorest resolution, best chemical speciation
neutron tomography	50 μm, 1024^3, 2 hrs	~6 beamlines worldwide, some in renovation, elemental sensitivity. US: NIST, UC Davis, **Spallation Neutron Source**
electron micro. tomo	2 nm, 512^3, ? hrs	in development; best sample geometry is a thin rod
microtome & 2D EM	2 x 2 x 50 nm, $>1024^3$, >12 hrs	labor intensive; problems with slice-to-slice alignment

Spallation Neutron Source

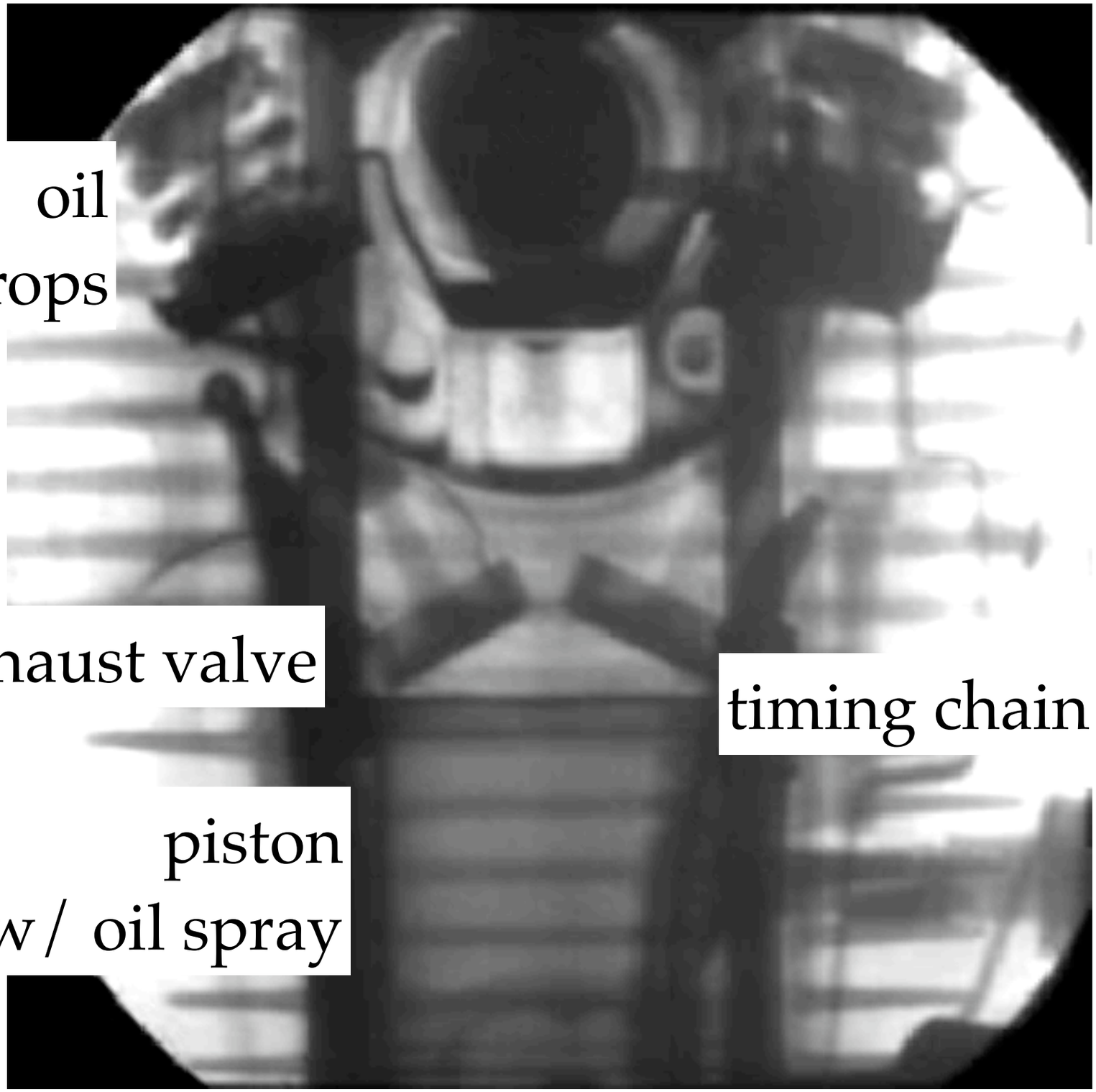
- Neutrons are produced at near-point source by the collision of high-energy protons with a Hg target: 695 ns pulse with 60 Hz rep. rate.
- The experimental hall is about 3/4-populated.
  Is there room for tomography?

Linear accelerator

Experimental hall

Examples of Radiography in Engineering

- FRM-II (Munich): air-cooled gas engine



This work uses back projection.

Plans to use discrete tomography for 3D movies.

Movie recorded at ILL by G. Frei (PSI), B. Schillinger (FRM-II), and A. Hillenbach (ILL), et al.

http://sns.gov

The Spallation Neutron Source is an accelerator-based neutron source in Oak Ridge, Tennessee, USA. At full power, the SNS will provide the most intense pulsed neutron beams in the world for scientific research and industrial development.

IAN2006

Imaging and Neutrons 2006

October 23-25, 2006
Oak Ridge, TN

IAN2006 is an international action-oriented workshop to

- Identify the current needs and potential contributions of imaging with neutrons in a wide range of science and areas of applications.
- Recognize new imaging techniques that may be made possible by advanced next generation sources that go beyond established techniques of radiography and tomography.
- Produce a report identifying both potentially valuable imaging techniques and directions for additional research and investment to realize this potential worldwide.

Applications areas

- Medical/Biomedical
- Molecular and Cellular Biology
- Chemistry
- Engineering
- Physics
- Geology
- Energy/Nuclear Power
- Materials Research
- Cultural Heritage
- Homeland Security
- Contraband Detection

Techniques

- Radiography
- Tomography
- Microscopy
- Holography
- Neutron Simulated Emission Computed Tomography
- Magnetic imaging
- Resonant imaging
- Bragg-edge imaging by Time of Flight
- Advanced reconstruction algorithms
- Other techniques to be identified

International Organizing Committee

D. Penumadu (University of Tennessee), Chair
C. Andreani (Università degli Studi di Roma Tor Vergata)
M. Arai (Japan Atomic Energy Agency)
W. Ball (University of Cincinnati)
L. Butler (Louisiana State University)
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www.sns.gov/workshops/ian2006

For additional information, contact: Al Ekkebus,ekkebusae@sns.gov, (865) 241-5644

Workshop supported by Oak Ridge National Laboratory, Spallation Neutron Source • Integrated Infrastructure Initiative for Neutron Scattering and Muon Spectroscopy (NMI3) • Oak Ridge Associated Universities • Joint Institute for Neutron Sciences in cooperation with the International Atomic Energy Agency

Source: (a) D. Schwarz et al., Paleontology Electronica (2003), Neutra Facility, PSI. (b) E. Lehmann et al., Neutra Facility, PSI. (c) W. Kockelmann, Applied Physics A 83 (2006), Neutrograph Facility, ILL. (d) E. Lehmann et al., Neutra Facility, PSI. (e) J. Brunner et al., Nuclear Instruments and Methods in Physics Research A 542 (2005), Neutrograph Facility, ILL.

http://sns.gov

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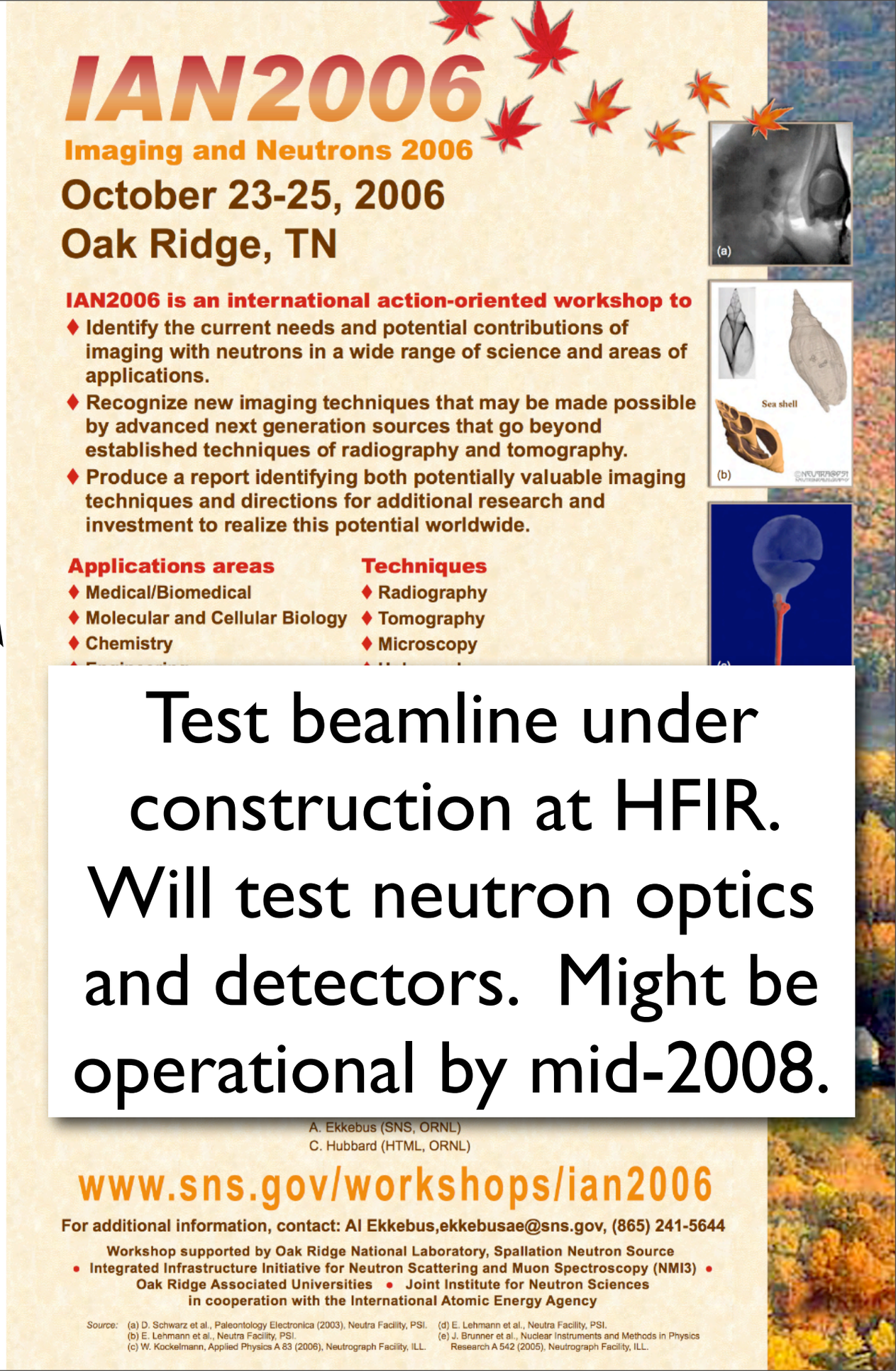
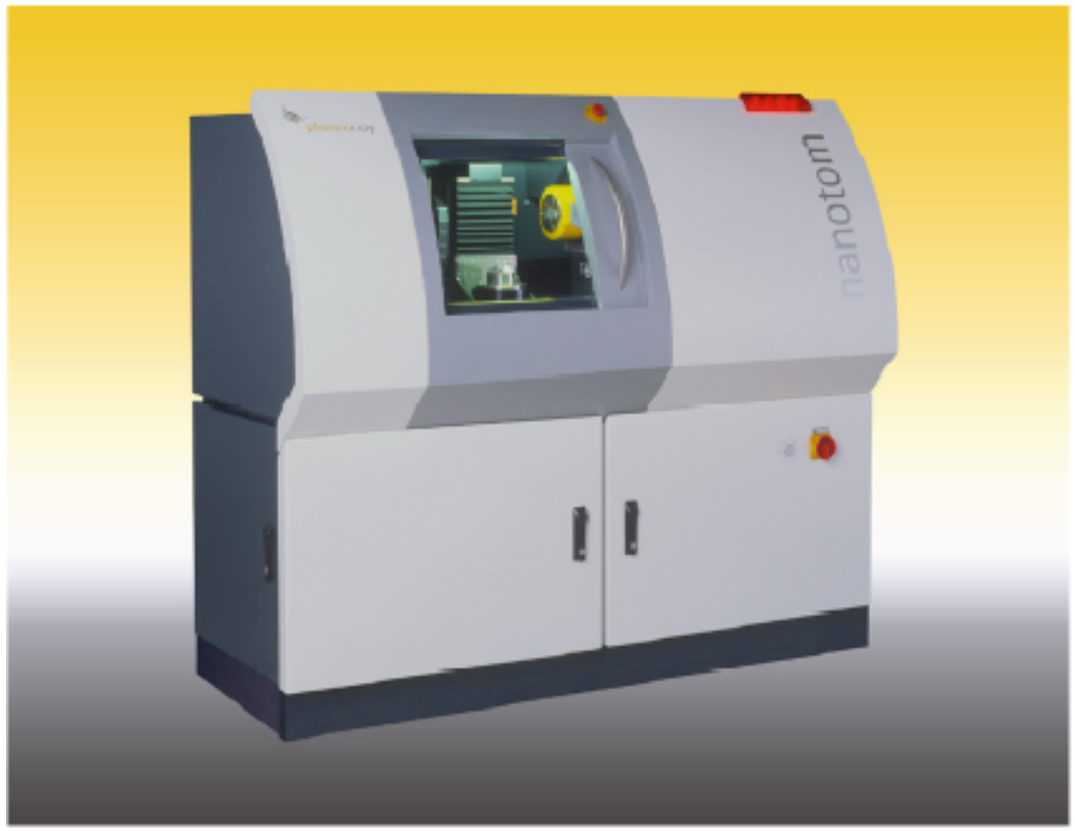


Test beamline under construction at HFIR. Will test neutron optics and detectors. Might be operational by mid-2008.

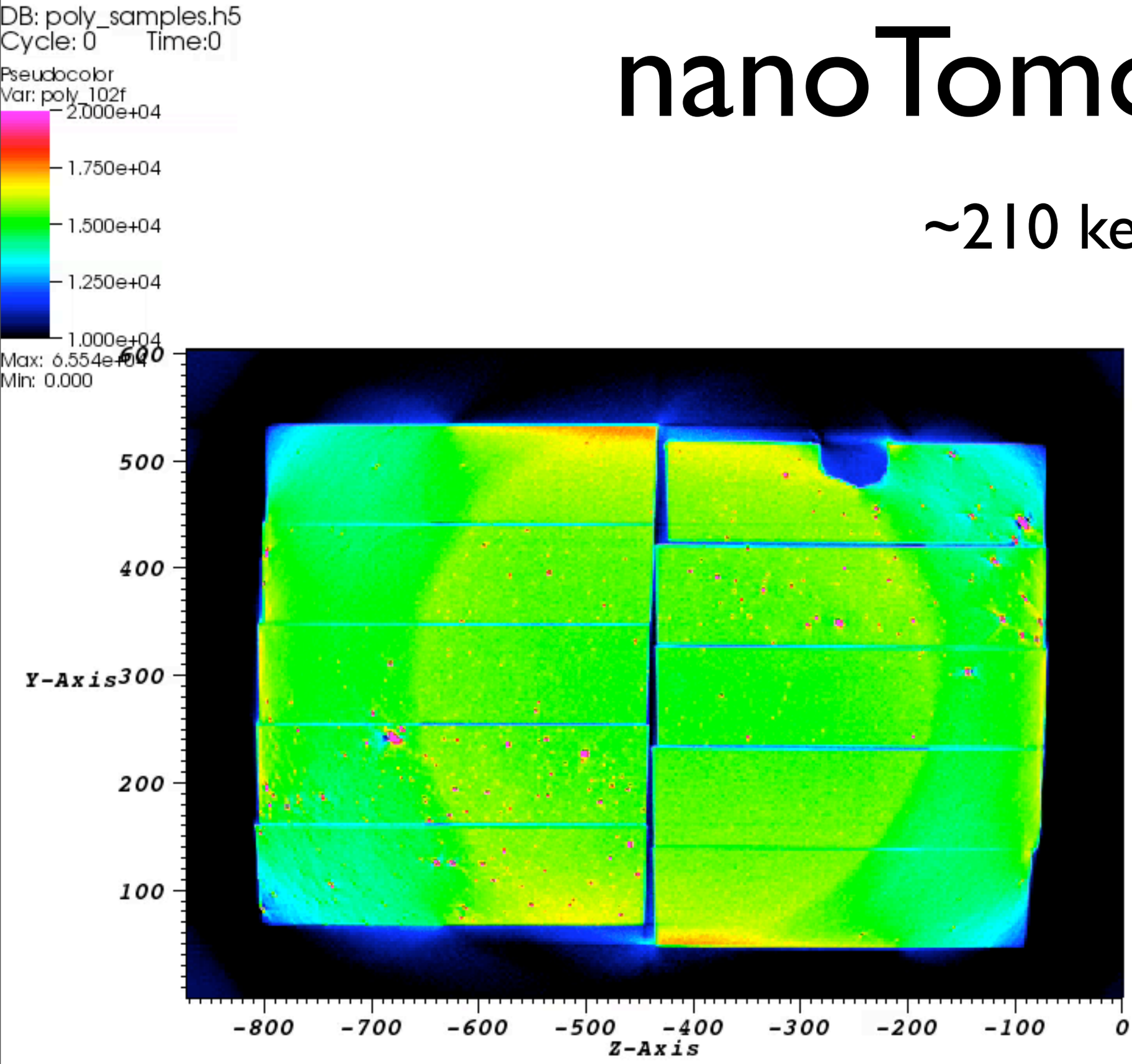
Lab tomography: the Phoenix X-ray nanoTom



99B	102F
99D	102D
99A	102A
99G	99J
99F	99H

nanoTomo

~210 keV, 34 µm



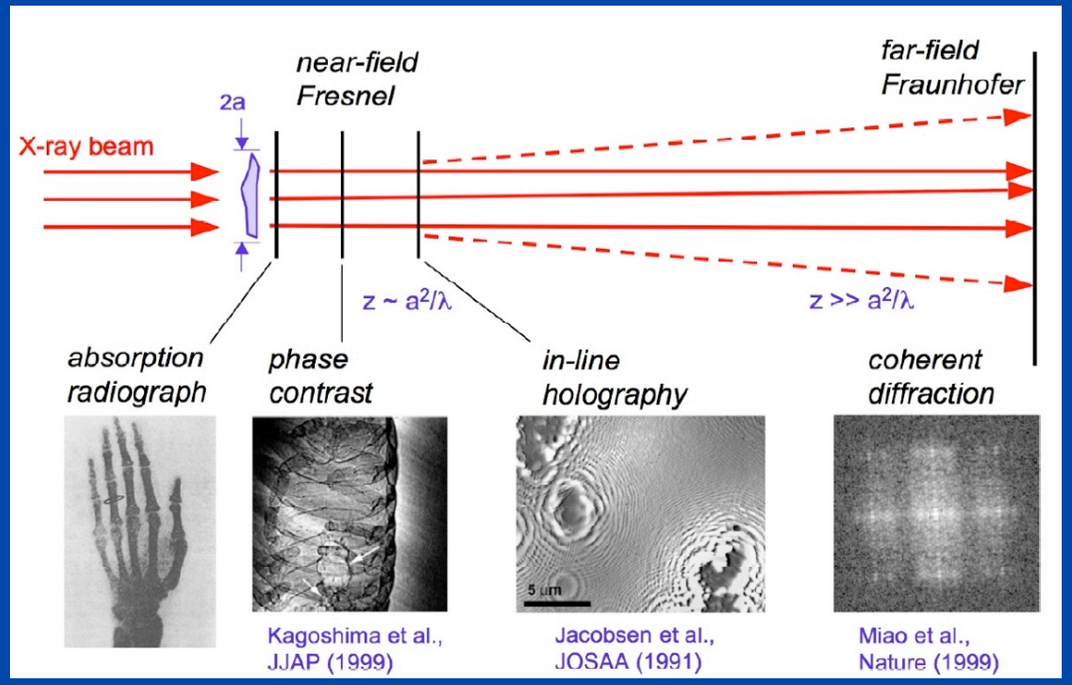
99F	99H
99G	99J
99A	102A
99D	102D
99B	102F

bottom up view

user: barnett
Thu May 24 14:37:58 2007

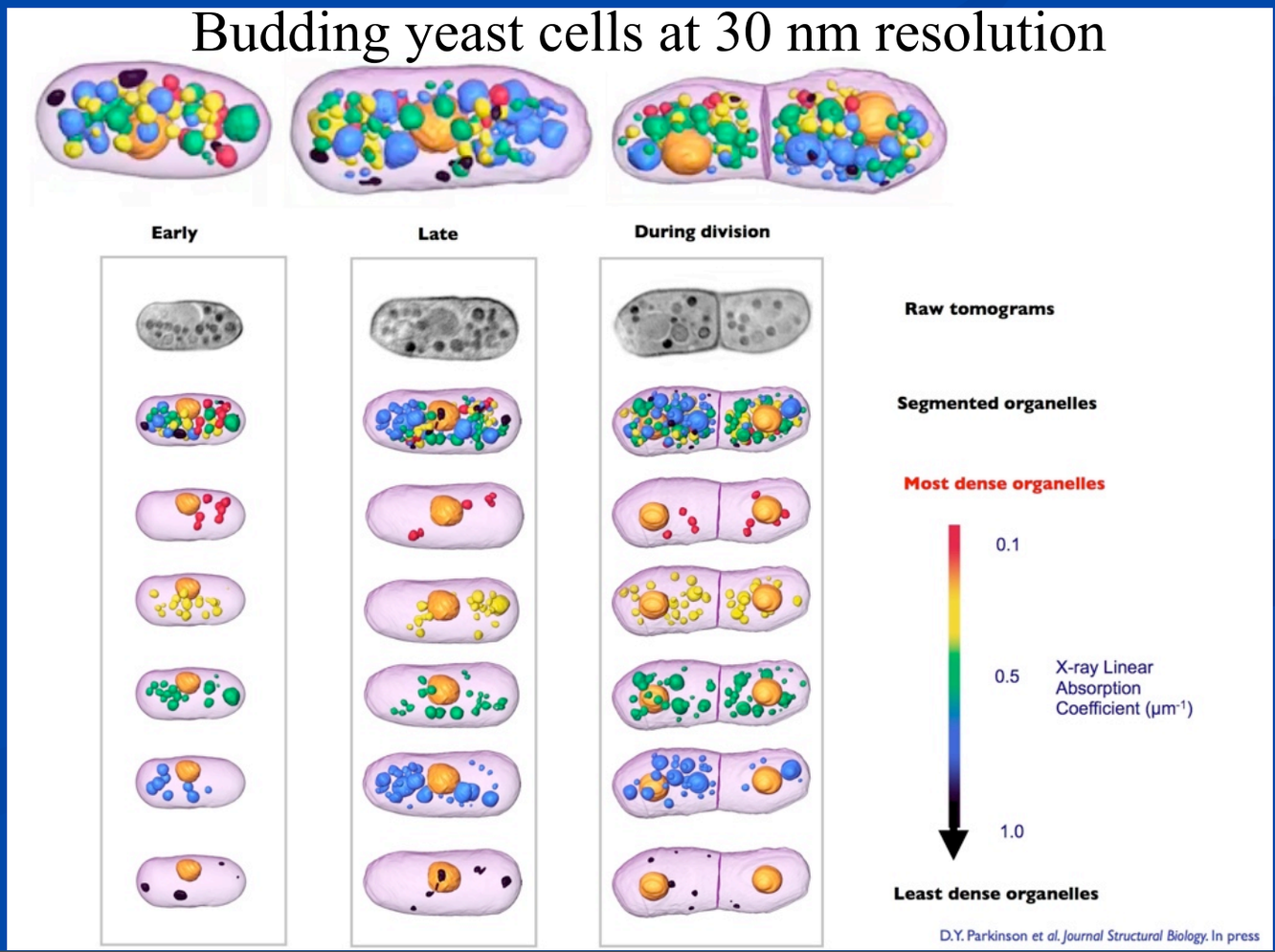
Tomography: future

- If DOE BESAC recommends 4-th gen. soft X-ray source (< 1 keV), then
  - Image biological cells at ~500 eV, the 'water window'. Full 3D volumes can be imaged at ~40 nm resolution today, and potentially to 10 to 15 nm. Concerns are X-ray flux damage to cell will require better projection reconstruction methods, better attention to sampling theory. (McDermott, ALS)
  - Many applications to polymer blends, composite materials, especially with coherent diffractive imaging
  - MHI-ers: ALS nanotomography: Carolyn Larabell, Gerry McDermott, (or from their groups), Ian McNulty (APS), Franz Pfeiffer (Swiss Light Source)



CAMD now: absorption & phase contrast

4-th gen. X-ray X-ray optics for ~10 nm resolution & coherent diffractive imaging



software stack (Ed)

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- huge metadate needs
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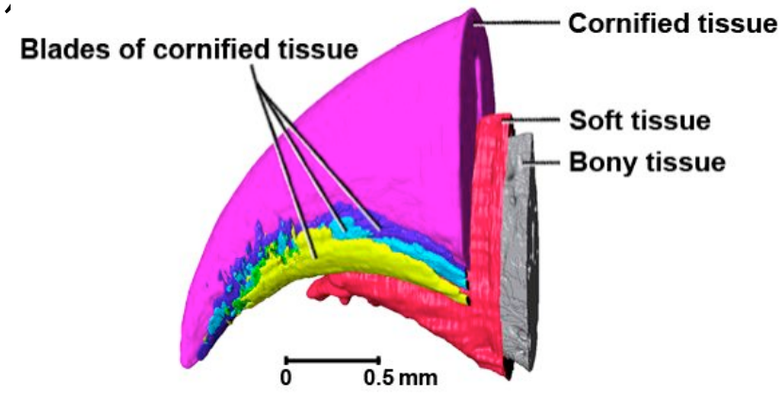
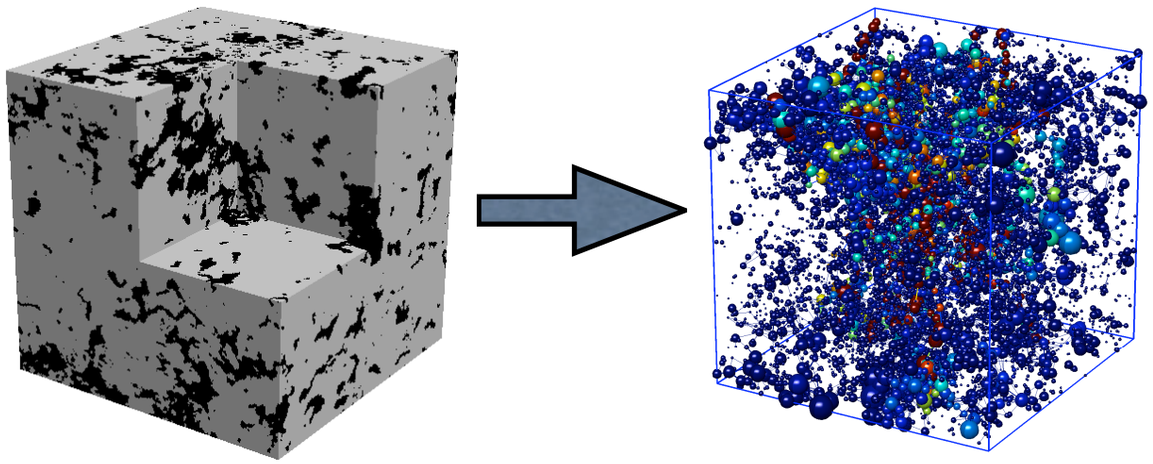
New structures in cat claws discovered with synchrotron X-ray tomography.
Homberger, 2007



Real sandstone samples provides authentic geometry for flow modeling. Applications range from environmental remediation to oil&gas recovery.
Thompson & Willson, 2008



flow rates
red = fast
blue = slow