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... for a brighter future

Your Synchrotron Powder Diffraction Instrument: 11-BM at Argonne's Advanced Photon Source

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U.S. Department of Energy

THE UNIVERSITY OF CHICAGO

Office of Science U.S. DEPARTMENT OF ENERGY

A U.S. Department of Energy laboratory managed by The University of Chicago

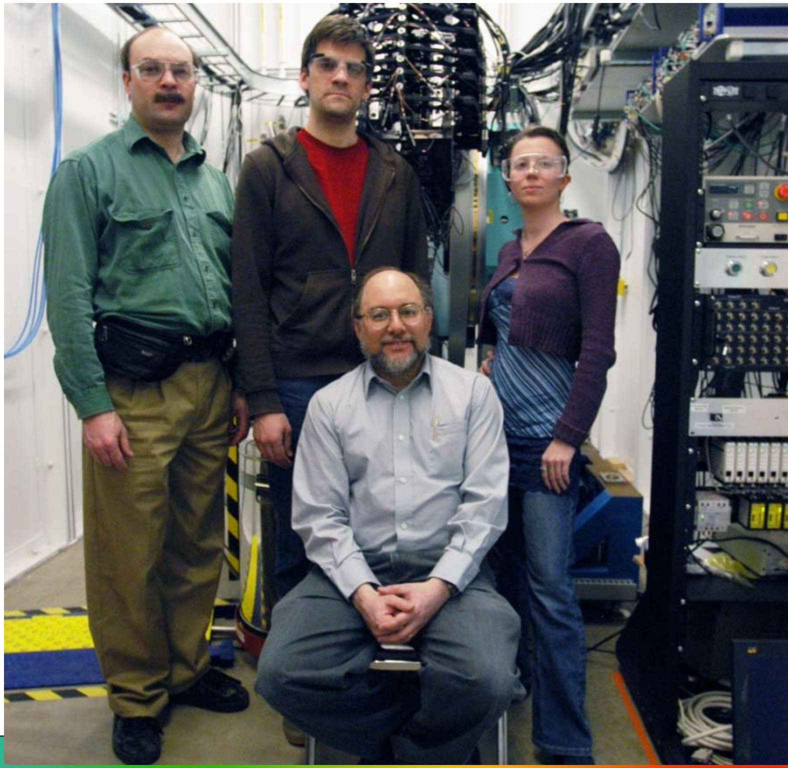
This document was presented at PPXRD - Pharmaceutical Powder X-ray Diffraction Symposium

Sponsored by The International Centre for Diffraction Data

Acknowledgements

- *11-BM staff:* **Matt Suchomel, Lynn Ribaud**, Bob Von Dreele (Jun Wang, Sytle Antao, Jennifer Doebbler)
- *Design & much more*: Mark Beno, Peter Lee, Mohan Ramanathan & Chuck Kurtz
- *Engineering*: Deming Shu, **Curt Preissner**, David Kline
- *Equipment protection*: Mark Engbretson
- *Instrument control*: **Xuesong Jiao** & Tim Mooney
- *Linux:* Bill Sheehan & Dave Cyl
- *Databases*: Don Dohan & Yu Huang
- *Web programming*; David Carroll

- John Mitchell for launching the project
  - Ray Orbach for listening to him



Talk outline

- **What** do you gain from powder diffraction at user facilities
- **Why** mail-in support?
- **What** does this require?
- **How** do you get access?
- **What** can be done with these data?

11-BM: High-throughput powder diffraction without compromise

Part 1: High resolution powder diffraction, the next generation

What do you gain from diffraction experiments at User Facilities?

- Neutrons: sensitive to many light atoms & provides excellent structural information
  - Few systematic errors
  - powder diffraction usually requires deuterium substitution
  - Short wavelength (TOF) – high Q
- Synchrotron:
  - High resolution
  - Short wavelength
  - High sensitivity

  or
  - Very rapid measurements (10 patterns/sec)

  or
  - Small beams (microns)

- ***Less overlap, more observations:*** **Better for structure solution; more accurate structures; subtle symmetry**
- ***More observations, fewer corrections:*** **more accurate…**
- **Subtle symmetry; minor phases**

- Both: *in situ* & extreme temperature conditions

Advantages of High-Resolution Powder Diffraction

- **High-resolution diffraction** - allows peaks to be resolved: essential for indexing and structure solution. Provides more observations: ***more reliable results***

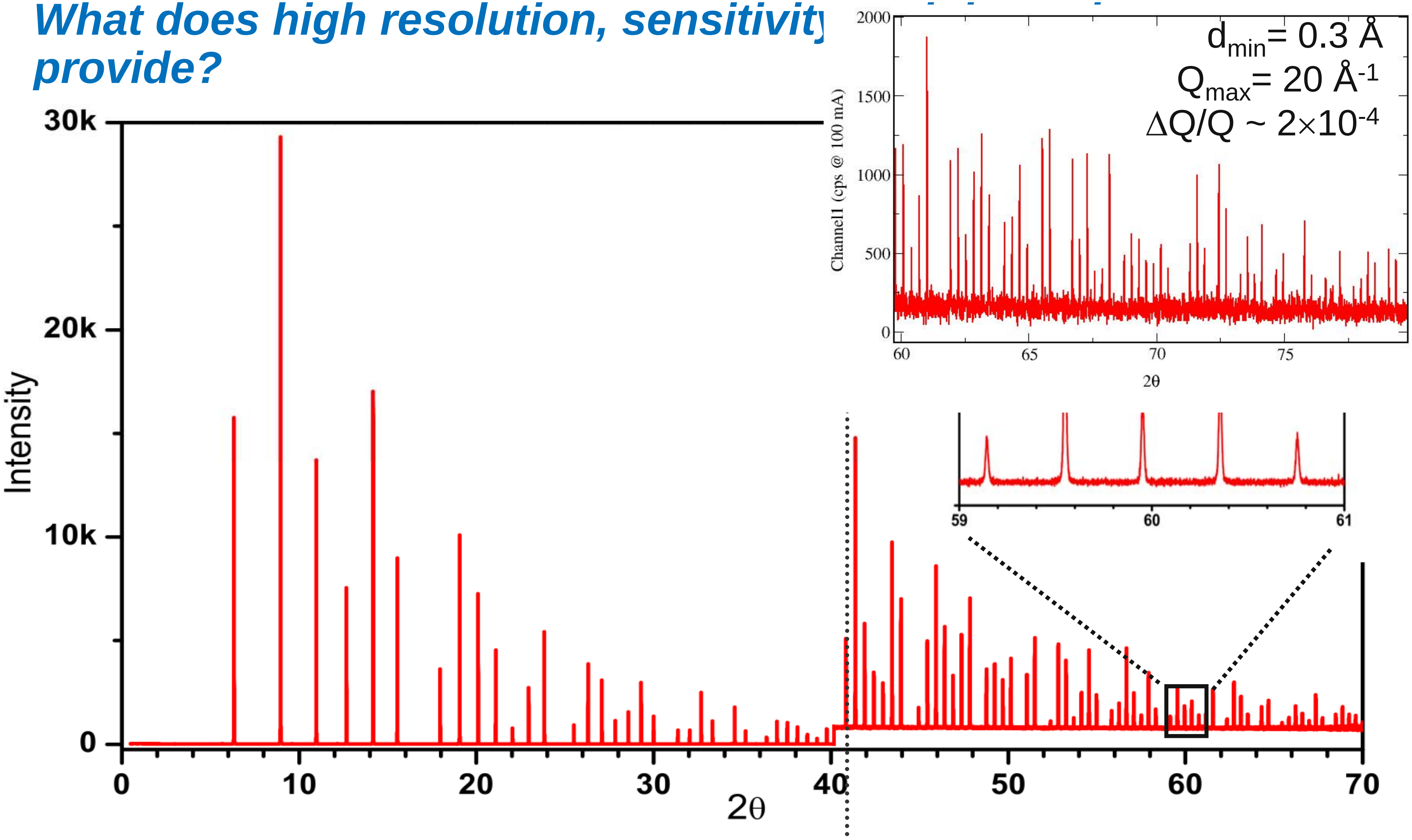
- **High-sensitivity diffraction** - allows weak peaks to be seen above background: essential for structural details (also more observations)

- **Short wavelength –** fewer systematic errors (absorption, extinction,…) – ***more accurate*** data. Wider Q range energy - ***more observations*****.**

- **No sample offset error –** ***no zero corrections.*** Great for indexing.

- **High-Throughput diffraction -** allows these capabilities to be made available to the appropriate research communities in chemistry, materials, condensed matter physics, geosciences, pharmaceutical science, structural biology…

What does high resolution, sensitivit provide?

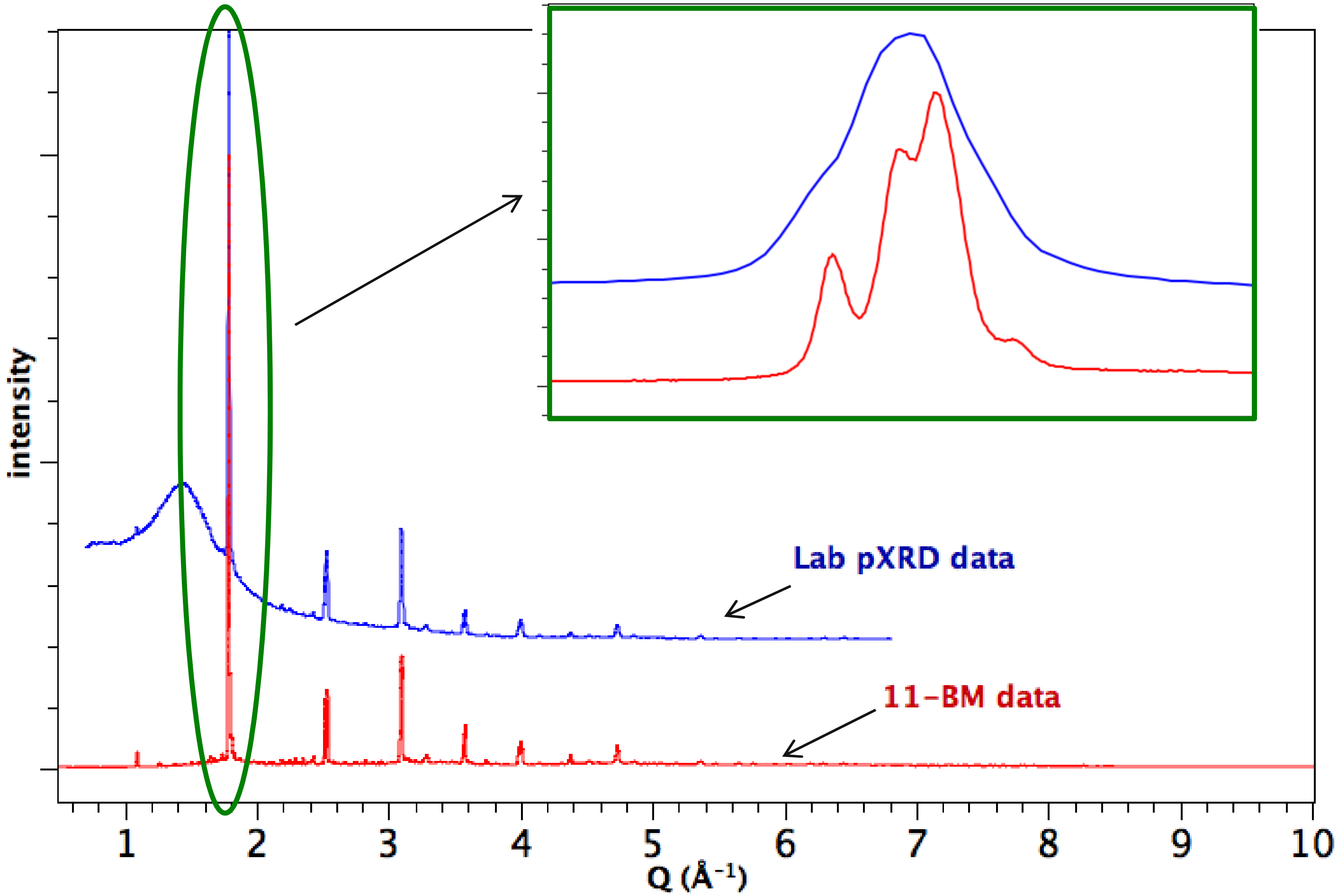


NIST SRM 660a (LaB_6) @ 27 keV (0.46 Å): 1 hour scan

11-BM: "Real World" examples I

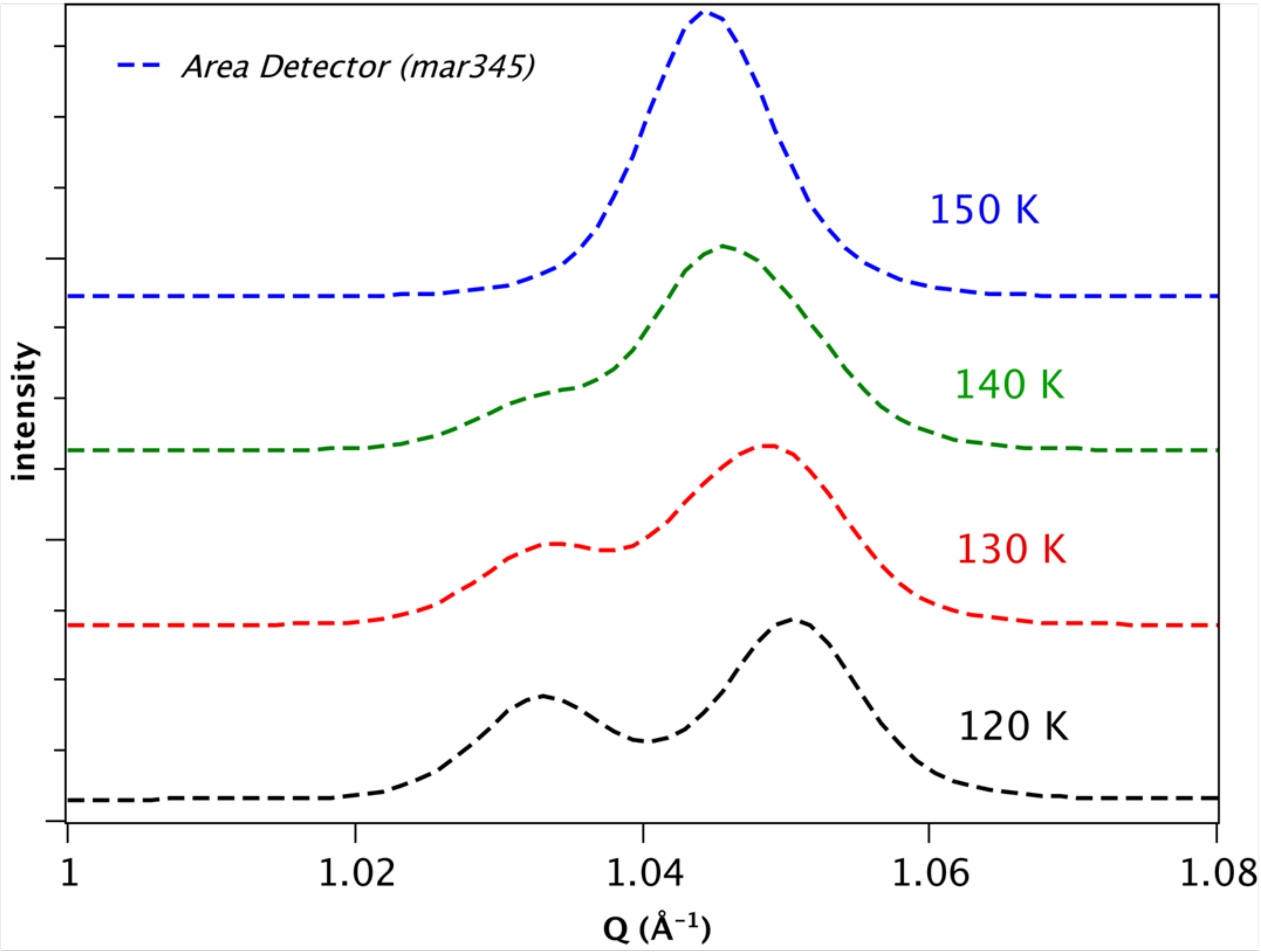
Air-sensitive Rare-Earth Fluoride; Lab pXRD vs 11BM (in sealed glass capillary)

→ better background, sensitivity, Q-range & resolution !

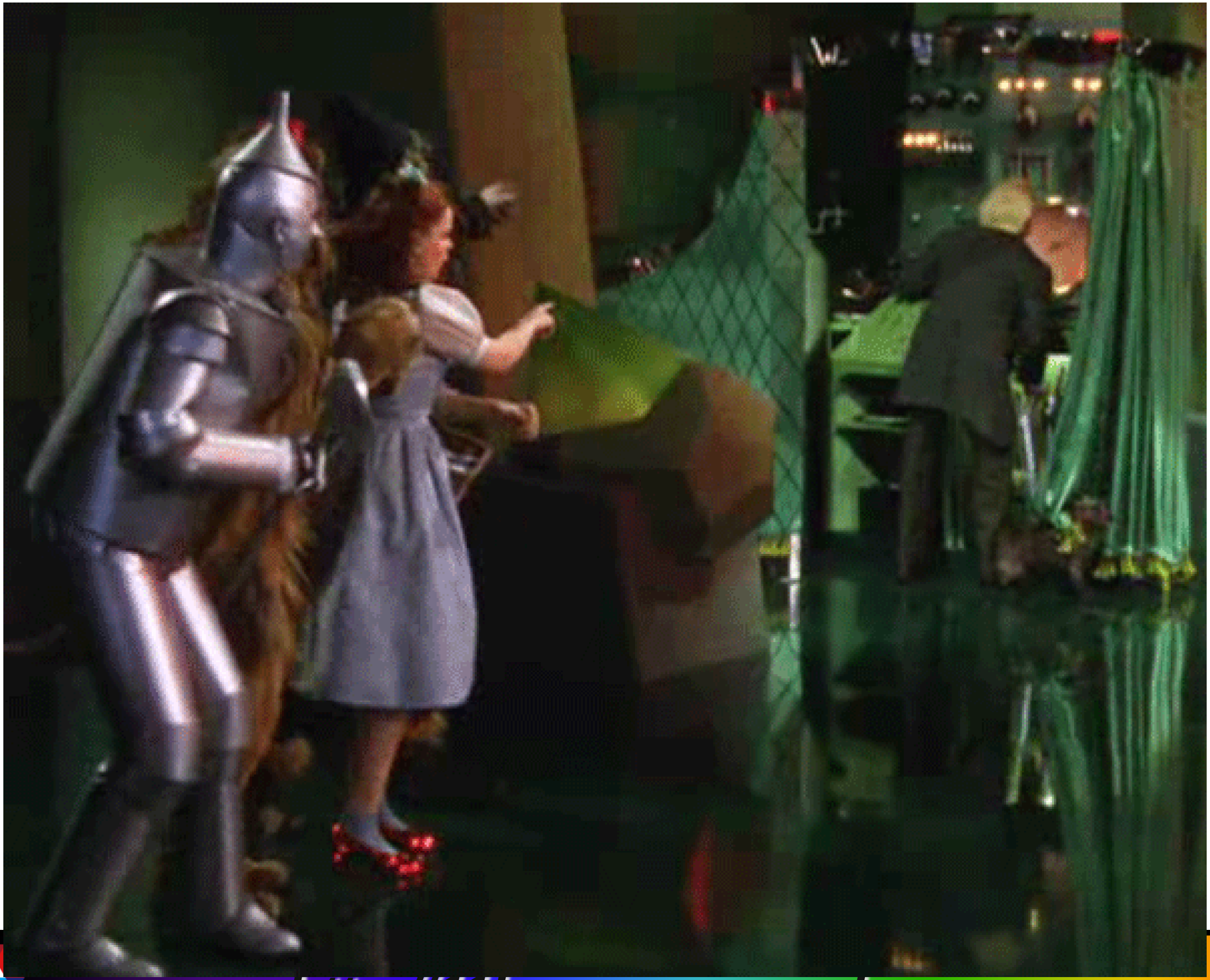


11-BM: "Real World" examples III

Structural Phase Transition in Organic-Inorganic Hybrid Material…

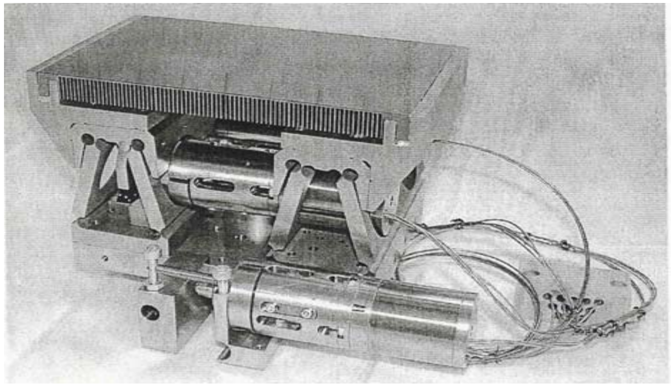


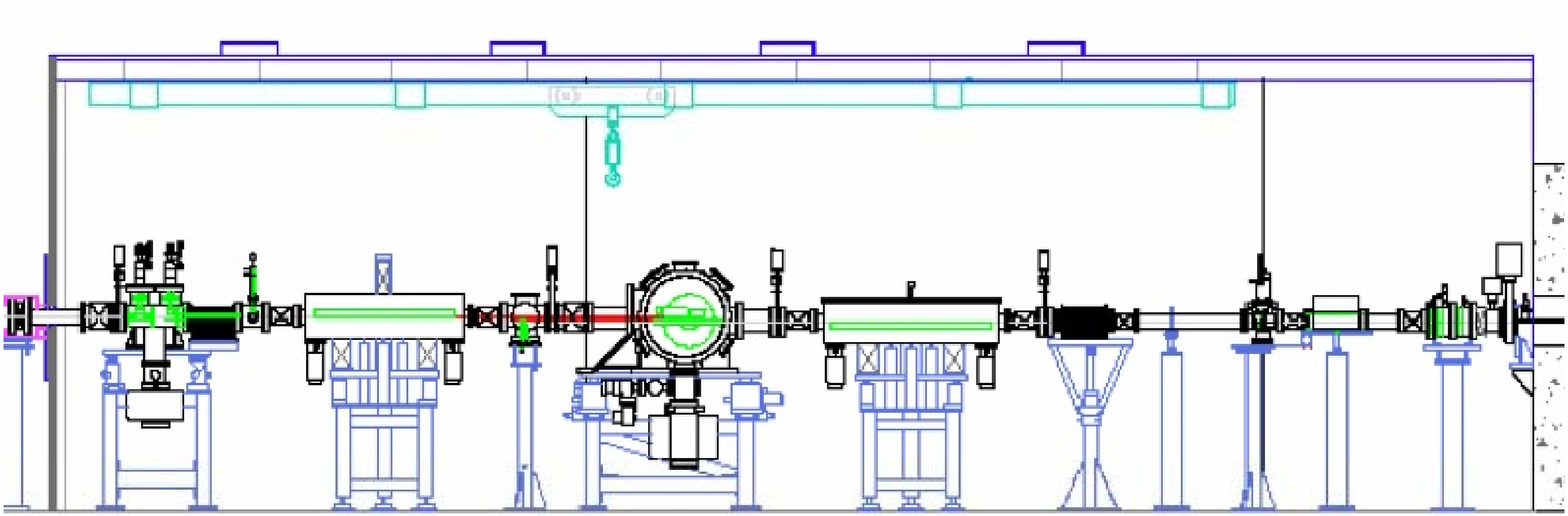
Part 2: Design of an instrument to support routine high resolution, high throughput and high sensitivity diffraction



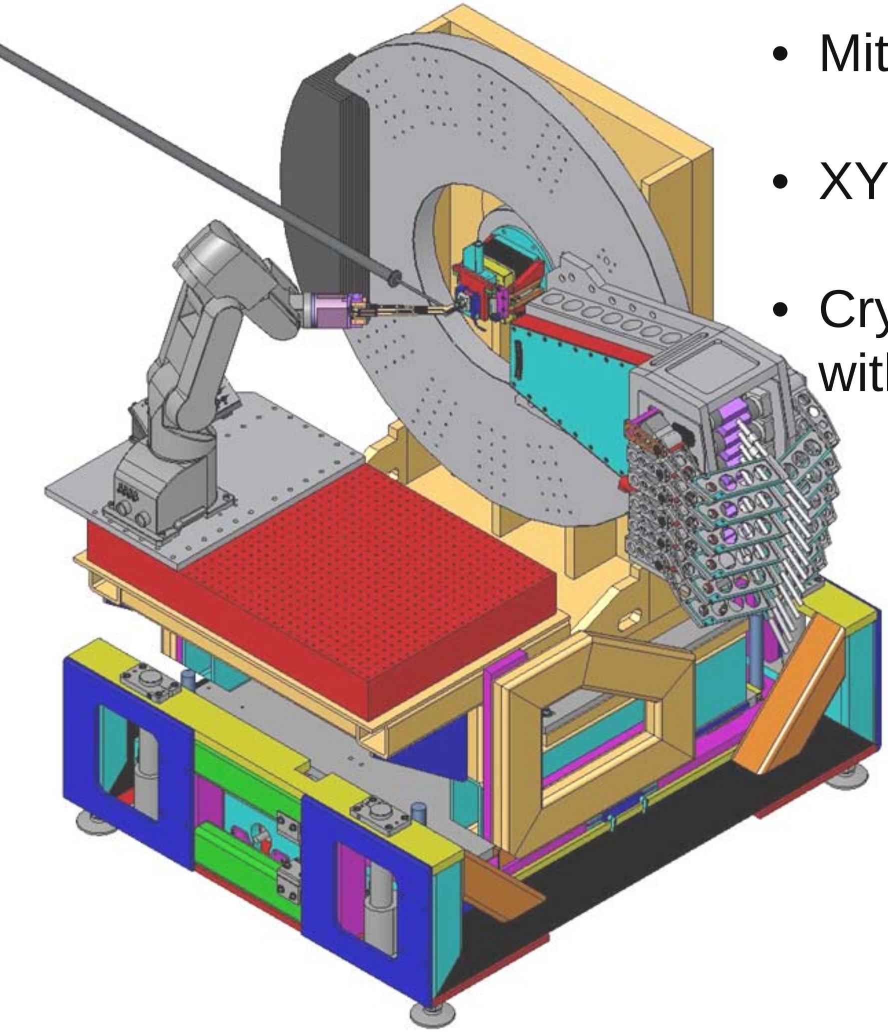
Beamline optics for high intensity and resolution

- Energy range – 5.5-39keV (2.5 – 0.3Å)
- Energy resolution – $\Delta E/E \sim 10^{-4}$
- 1:1 sagittal focusing (optimal resolution)





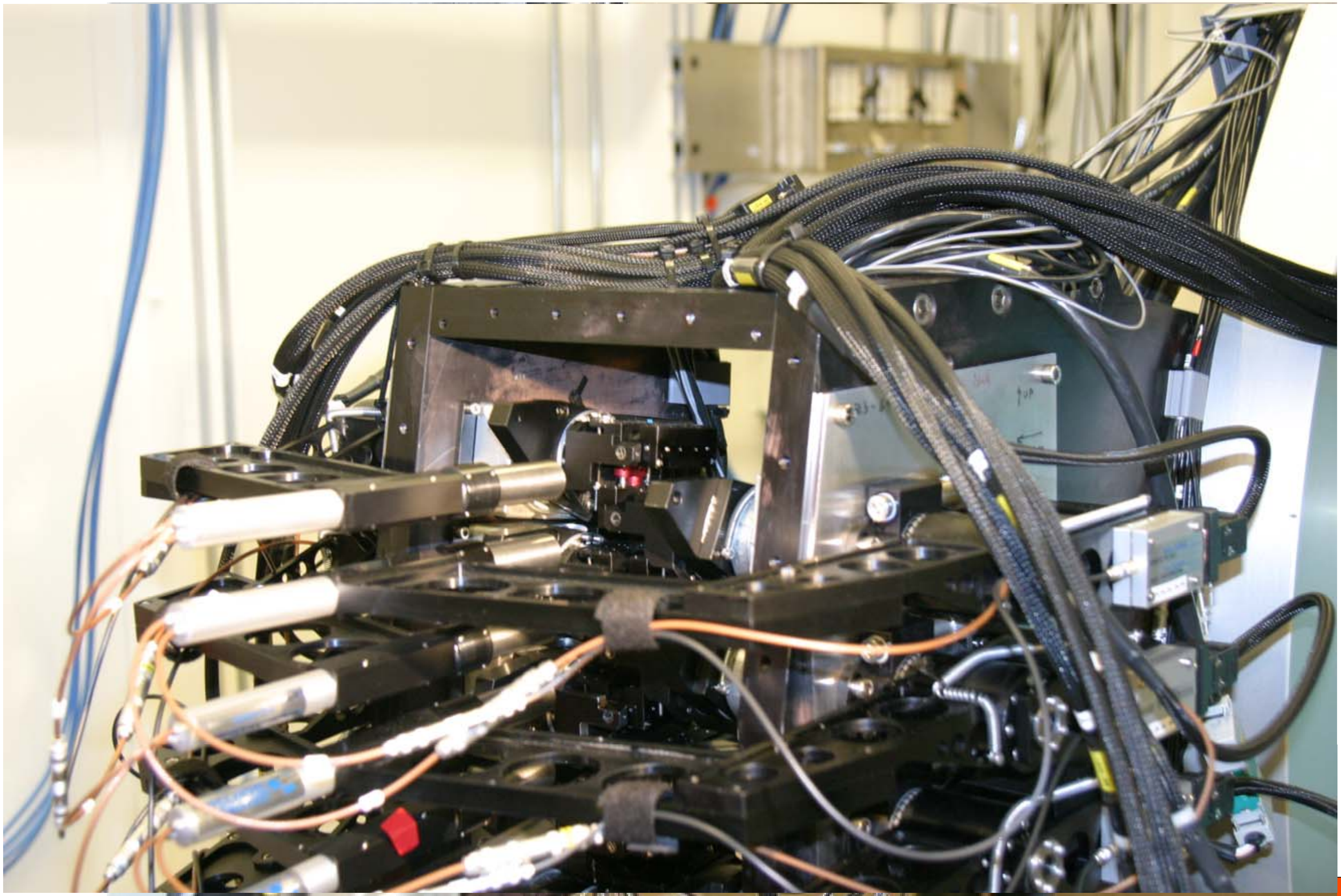
Instrument:



- 12 crystal two-axis analyzer detector – speed data collection
- Mitsubishi robot – unattended operation
- XYZ stage w/high speed spinner
- Cryostream 700+ -- unattended operation with data collection at 80 to 500 K

12 Analyzer/Detector System

As assembled



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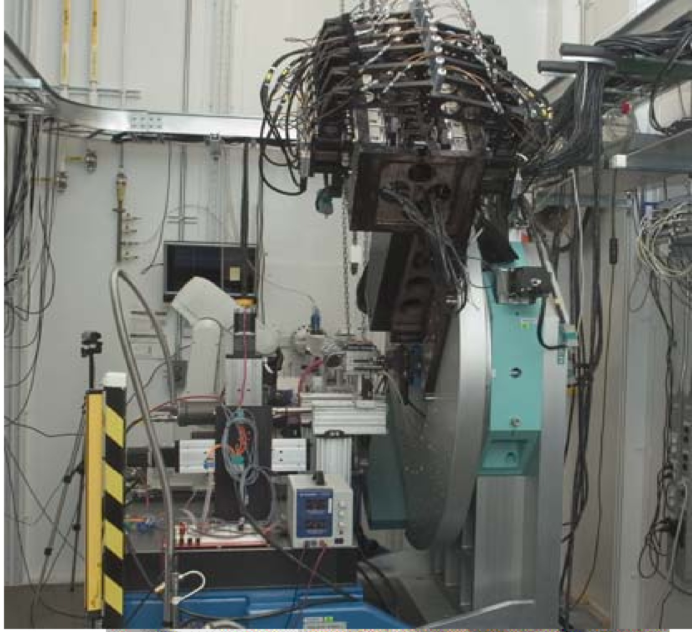
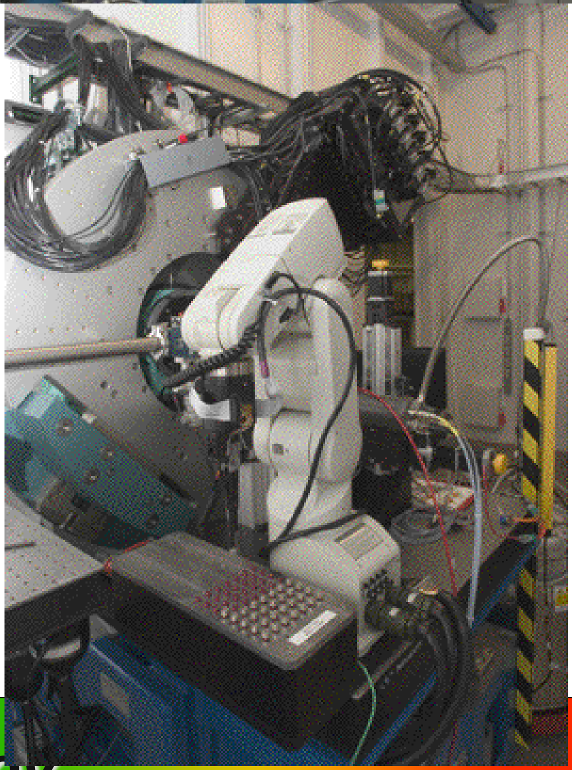
Make it easy to use



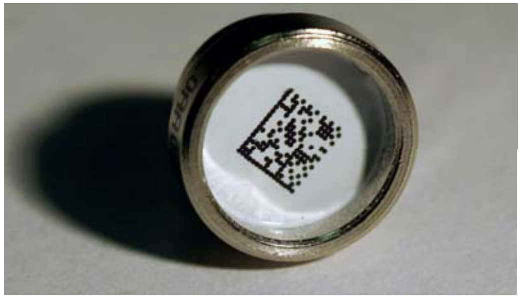
For facile and routine access automation requires:

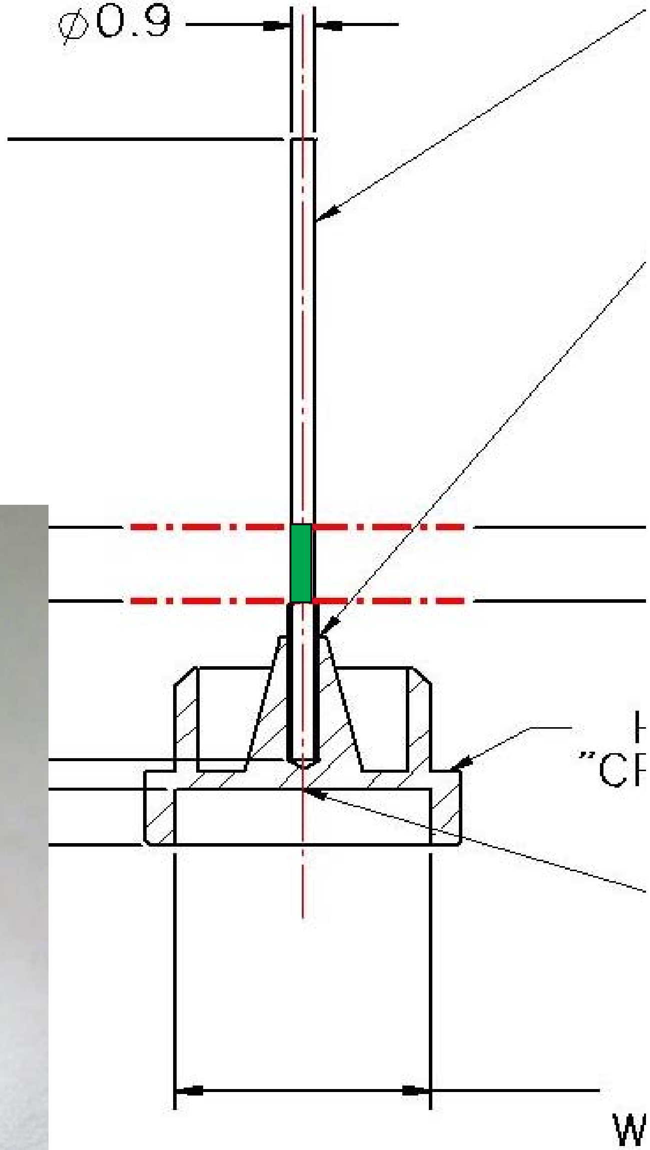
1. Must get many (>20) samples through per day
2. Resolution must be best available
3. Software must track samples and manage data
4. Software must be web-based and easy to use



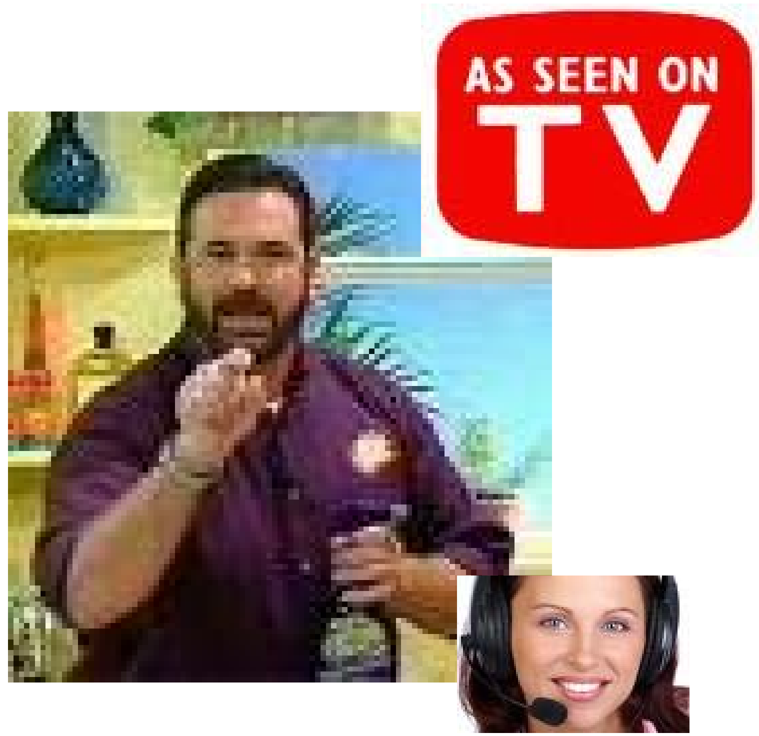
Standardized Sample Mounting

- We supply sample mounting kits with polyimide tubing and barcode.
  - Users fill tube and ensure the their sample fills and is fixed in the green area.
  - As long as sample tube remains straight, the sample is automatically placed in the beam





Part 3: Getting Access to 11-BM: The Infomercial



User'

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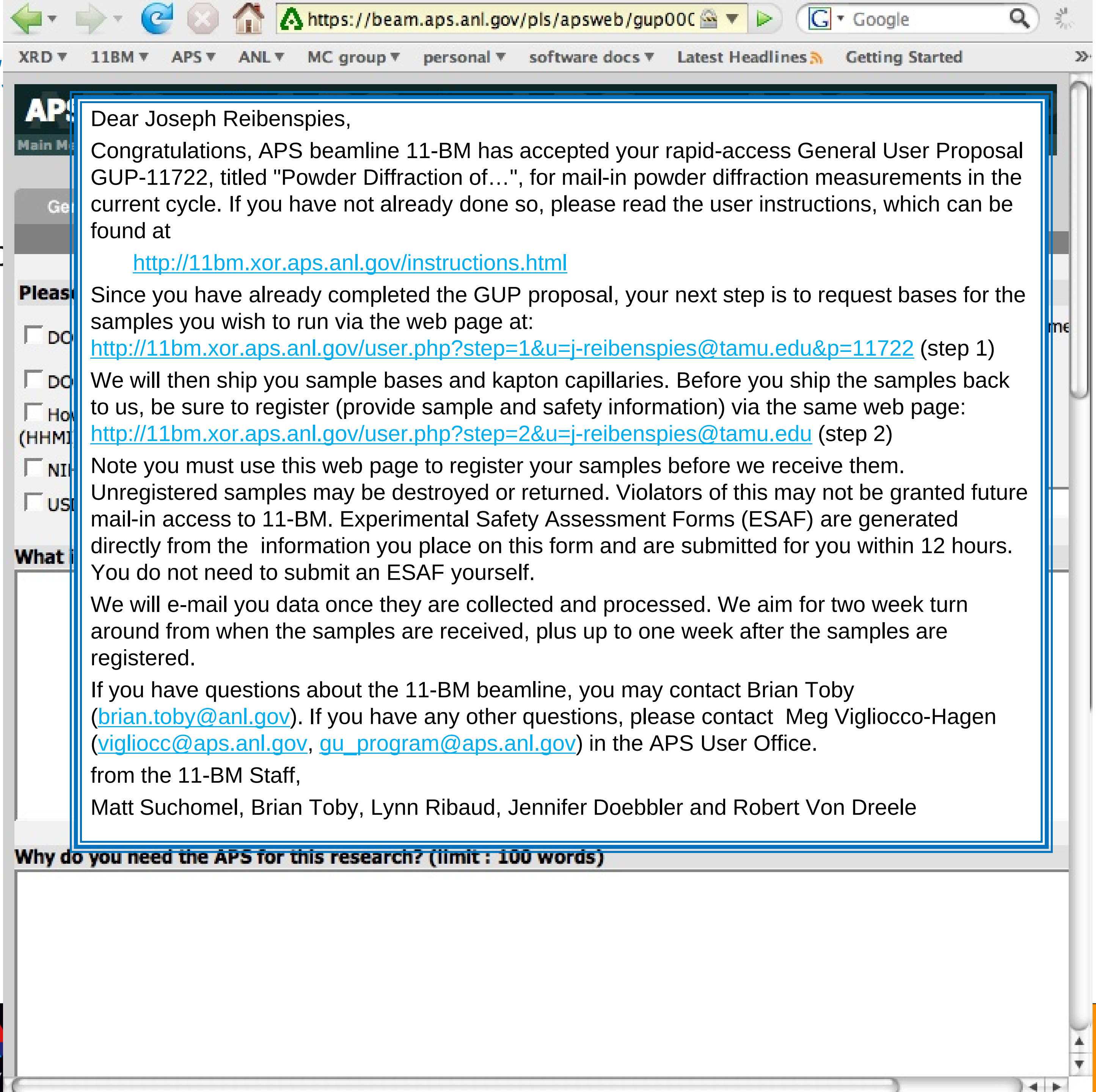

Dear Joseph Reibenspies,

Congratulations, APS beamline 11-BM has accepted your rapid-access General User Proposal GUP-11722, titled "Powder Diffraction of…", for mail-in powder diffraction measurements in the current cycle. If you have not already done so, please read the user instructions, which can be found at

http://11bm.xor.aps.anl.gov/instructions.html

Since you have already completed the GUP proposal, your next step is to request bases for the samples you wish to run via the web page at: http://11bm.xor.aps.anl.gov/user.php?step=1&u=j-reibenspies@tamu.edu&p=11722 (step 1)

We will then ship you sample bases and kapton capillaries. Before you ship the samples back to us, be sure to register (provide sample and safety information) via the same web page: http://11bm.xor.aps.anl.gov/user.php?step=2&u=j-reibenspies@tamu.edu (step 2)

Note you must use this web page to register your samples before we receive them. Unregistered samples may be destroyed or returned. Violators of this may not be granted future mail-in access to 11-BM. Experimental Safety Assessment Forms (ESAF) are generated directly from the information you place on this form and are submitted for you within 12 hours. You do not need to submit an ESAF yourself.

We will e-mail you data once they are collected and processed. We aim for two week turn around from when the samples are received, plus up to one week after the samples are registered.

If you have questions about the 11-BM beamline, you may contact Brian Toby (brian.toby@anl.gov). If you have any other questions, please contact Meg Vigliocco-Hagen (vigliocc@aps.anl.gov, gu_program@aps.anl.gov) in the APS User Office.

from the 11-BM Staff,

Matt Suchomel, Brian Toby, Lynn Ribaud, Jennifer Doebbler and Robert Von Dreele

Why do you need the APS for this research? (limit : 100 words)

User's ey

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2. Pr

Dear 11-BM user,

Please read the information below carefully as it pertains to obtaining access to 11-BM for pro

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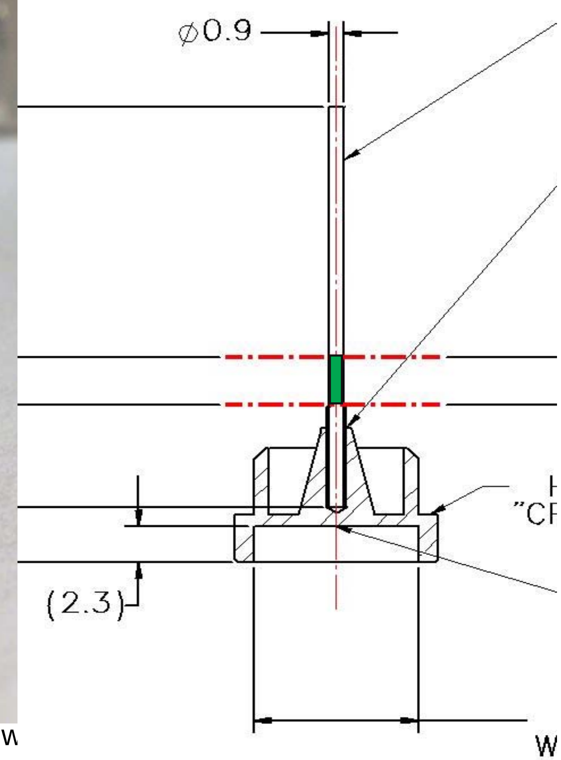

You
(8 hours) on 11-BM on this proposal have been approved. This request is w
allocation and will be processed when the URL above is used.

Thanks,the 11-BM team

Use

1. Su
2. Pr
3. Us

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Advanced Photon Source (APS)
General User Interface for 11-BM Mail-In Access

11-BM Sample Registration

There are 7 samples that have been logged to e-mail address `brian.toby@anl.gov` where sample information has not been registered; all unregistered samples are listed below.

Please input information into the boxes below. If all samples do not have the same safety information, fill out the safety information for the first sample listed and then leave blank the rows for any samples with differing classifications. For links describing the terms used below, see hazard definitions. A chemical formula, name, and a safety classification is required for each sample that will be sent for measurement at 11-BM.

Safety

Check here ☐ to indicate these material(s) qualify for the DOT small quantity exemption.

List sample-related hazards here:

☐ No hazards

☐ Toxic	☐ Carcinogen	☐ Flammable	☐ Corrosive	☐ Oxidizer	☐ Radioactive	☐ Human Origin	☐ Regulated Soil	☐ Explosive	N ▾ Biohazard
☐ Other, specify:									

Samples

#	Barcode	Collection Temperature	Chemical Formula	Chemical Name	Sample ID (optional)
1	ANL0AA0534	Ambient ▾			
2	ANL0AA0535	Ambient ▾			

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User's eye view of 11-BM proposal/sample systems

1. Submit an APS general user proposal.
2. Proposal is accepted
3. User supplies sample & safety information for each barcode
4. User sends mounted samples to APS

Send 11-BM Data

http://11bm.xor.aps.anl.gov/user.php?mode=senddata1&e

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Advanced Photon Source (APS)
General User Interface for 11-BM Mail-In Access

Send 11-BM Data: Select Files to be sent

On this form, select the samples for which you will want to receive data. The files will then be e-mailed to you in one or more zip-compressed data files or will be posted on a ftp server, at your option. Note that you can set the maximum size for each zip archive below. Also below, select the type of data files you want to get. After submitting the form, you will then get an e-mail message with a link. Use that link in a web browser to initiate the sending/posting of the files.

Displaying 22 of 22 sample(s) collected since 1/Jan/2008 for brian.toby@anl.gov

- Select file format(s) to be sent (documentation on file types):
  ☐ Send MDA files ☐ Send ASC files ☑ Send GSAS files ☐ Send TOPAS files ☐ Send CIF files
- Maximum zip file size: 5 Mb.
- ☐ Send all files below ◉ Send in email ○ Post on ftp site

#	Send File	Barcode	T (K)	Datafile Name	Date & Time Completed	Calibration File	Calibrated Wavelength
1	☐	ANL0AA1039	295	feb08/11bmb_0001.mda	2008-02-13 19:14:13		
2	☐	ANL0AA1039	295	feb08/11bmb_0002.mda	2008-02-14 11:47:06	feb08/11bmb_0003.calib	0.401096
3	☐	ANL0AA1038	295	feb08/11bmb_0004.mda	2008-02-14 14:08:21	feb08/11bmb_0003.calib	0.401096
4	☐	ANL0AA1036	295	feb08/11bmb_0005.mda	2008-02-14 15:20:10	feb08/11bmb_0003.calib	0.401096
5	☐	ANL0AA1027	295	feb08/11bmb_0006.mda	2008-02-14 16:31:50	feb08/11bmb_0003.calib	0.401096
6	☐	ANL0AA1030	295	feb08/11bmb_0007.mda	2008-02-14 17:43:31	feb08/11bmb_0003.calib	0.401096

Done

Us

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2.
3.
4.
5.

User's eye view of 11-BM proposal/sample systems

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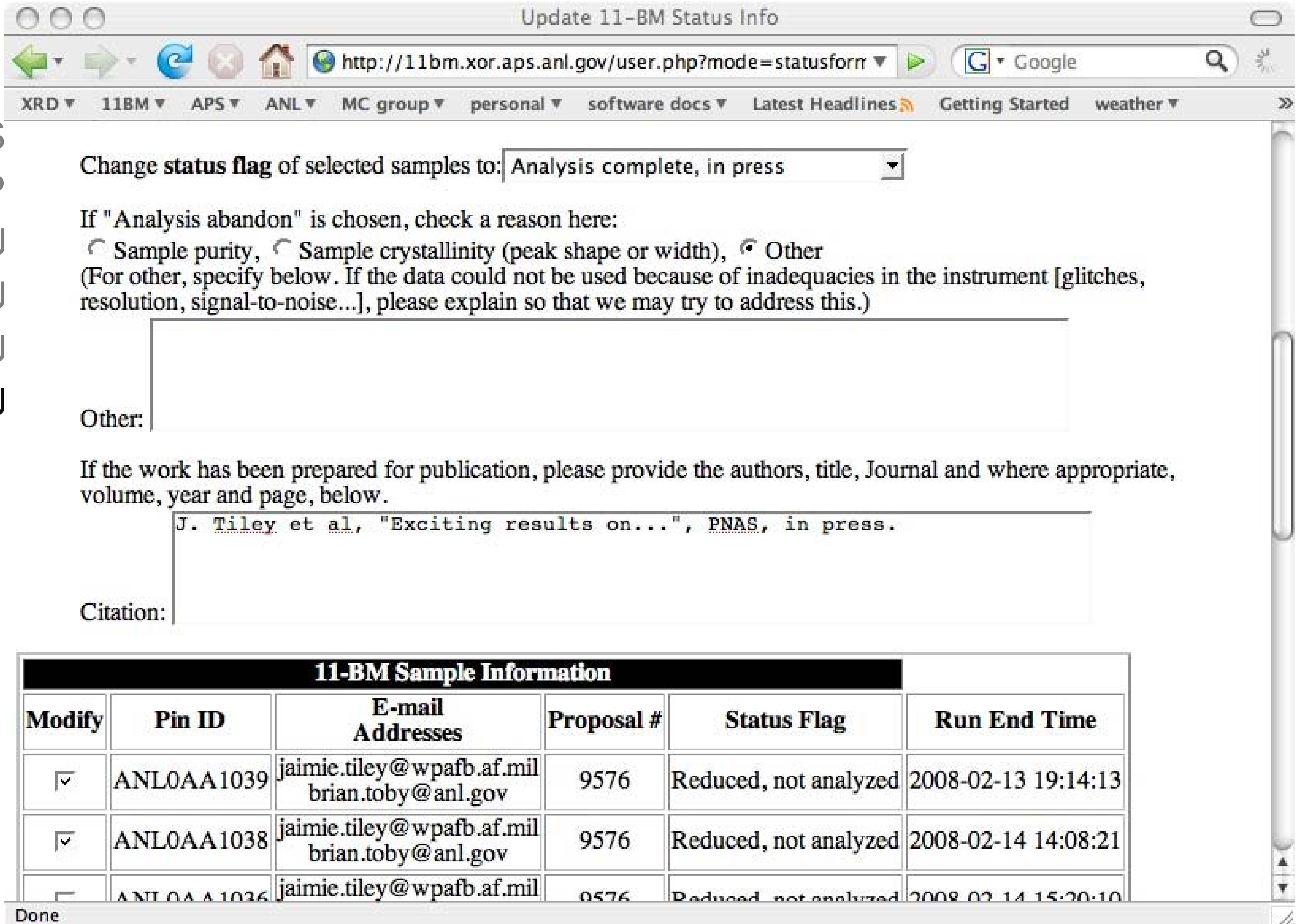
6. U



Update 11-BM Status Info

http://11bm.xor.aps.anl.gov/user.php?mode=statusform

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Change **status flag** of selected samples to: Analysis complete, in press

If "Analysis abandon" is chosen, check a reason here:
Sample purity, Sample crystallinity (peak shape or width), Other
(For other, specify below. If the data could not be used because of inadequacies in the instrument [glitches, resolution, signal-to-noise...], please explain so that we may try to address this.)

Other:

If the work has been prepared for publication, please provide the authors, title, Journal and where appropriate, volume, year and page, below.

Citation: J. Tiley et al, "Exciting results on...", PNAS, in press.

11-BM Sample Information

Modify	Pin ID	E-mail Addresses	Proposal #	Status Flag	Run End Time
☑	ANL0AA1039	jaimie.tiley@wpafb.af.mil brian.toby@anl.gov	9576	Reduced, not analyzed	2008-02-13 19:14:13
☑	ANL0AA1038	jaimie.tiley@wpafb.af.mil brian.toby@anl.gov	9576	Reduced, not analyzed	2008-02-14 14:08:21
☐	ANL0AA1036	jaimie.tiley@wpafb.af.mil	9576	Reduced, not analyzed	2008-02-14 15:20:10

Done

What does it cost?

- Non-proprietary work: **Free**
- Proprietary: US law requires cost recovery, <$400/hour

How long does it take?

- Most users receive sample bases within a week of proposal submission
- Most data is collected within a week (almost always within two weeks) of when the samples reach us.

Note that completion of paperwork (DOE User Agreement) is required for proposal submission. This can take some time, so this is good to start this in advance.

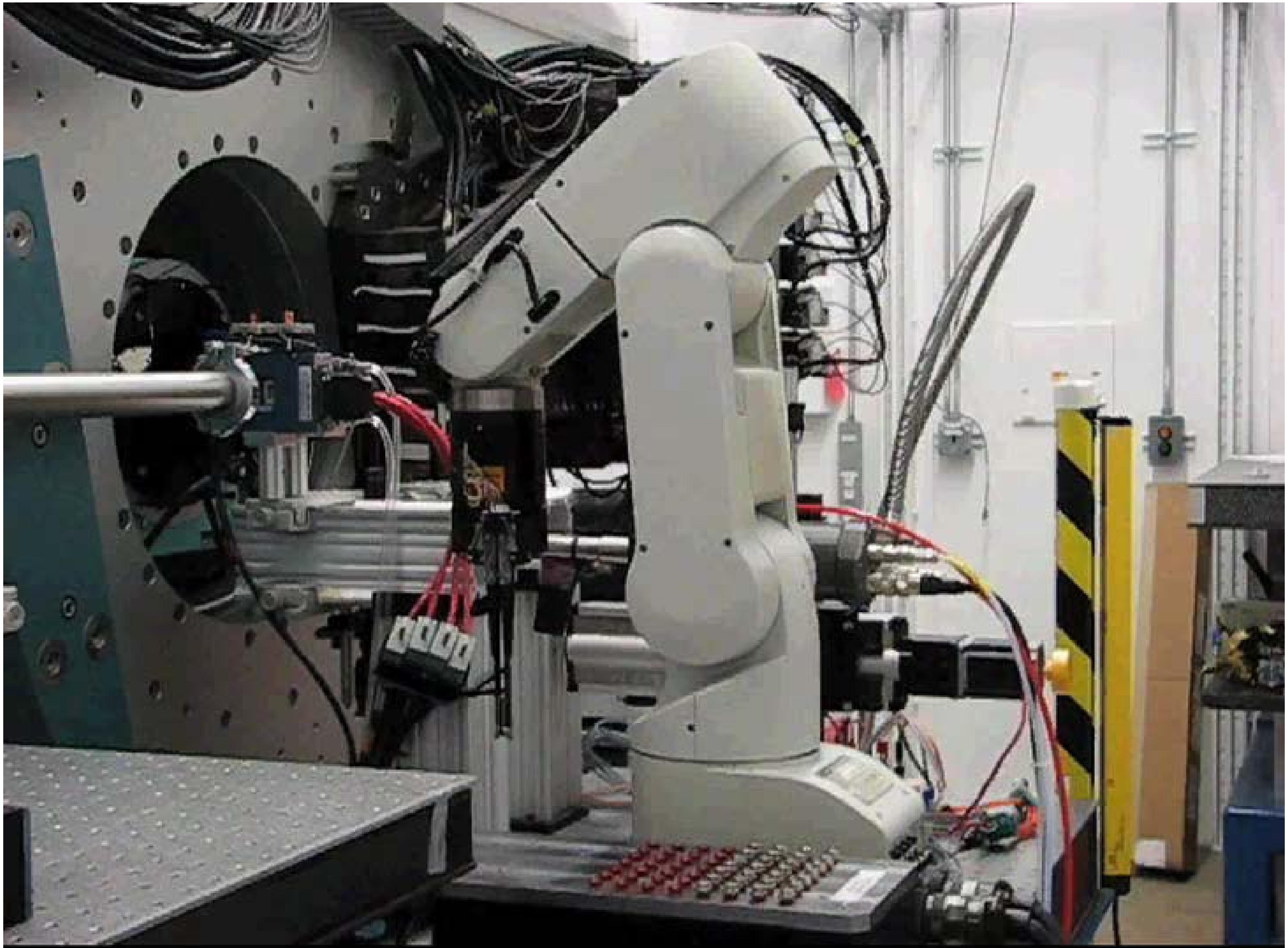
What's new: On-Site Use

Experimenters who have more extensive measurements, or ones where direct control of data collection

- High temperature (>200 C) or complex measurement protocols
  - When available: low T (<90 K)
- Large numbers of samples
- Non-routine sample mounts
- *In situ* experiments

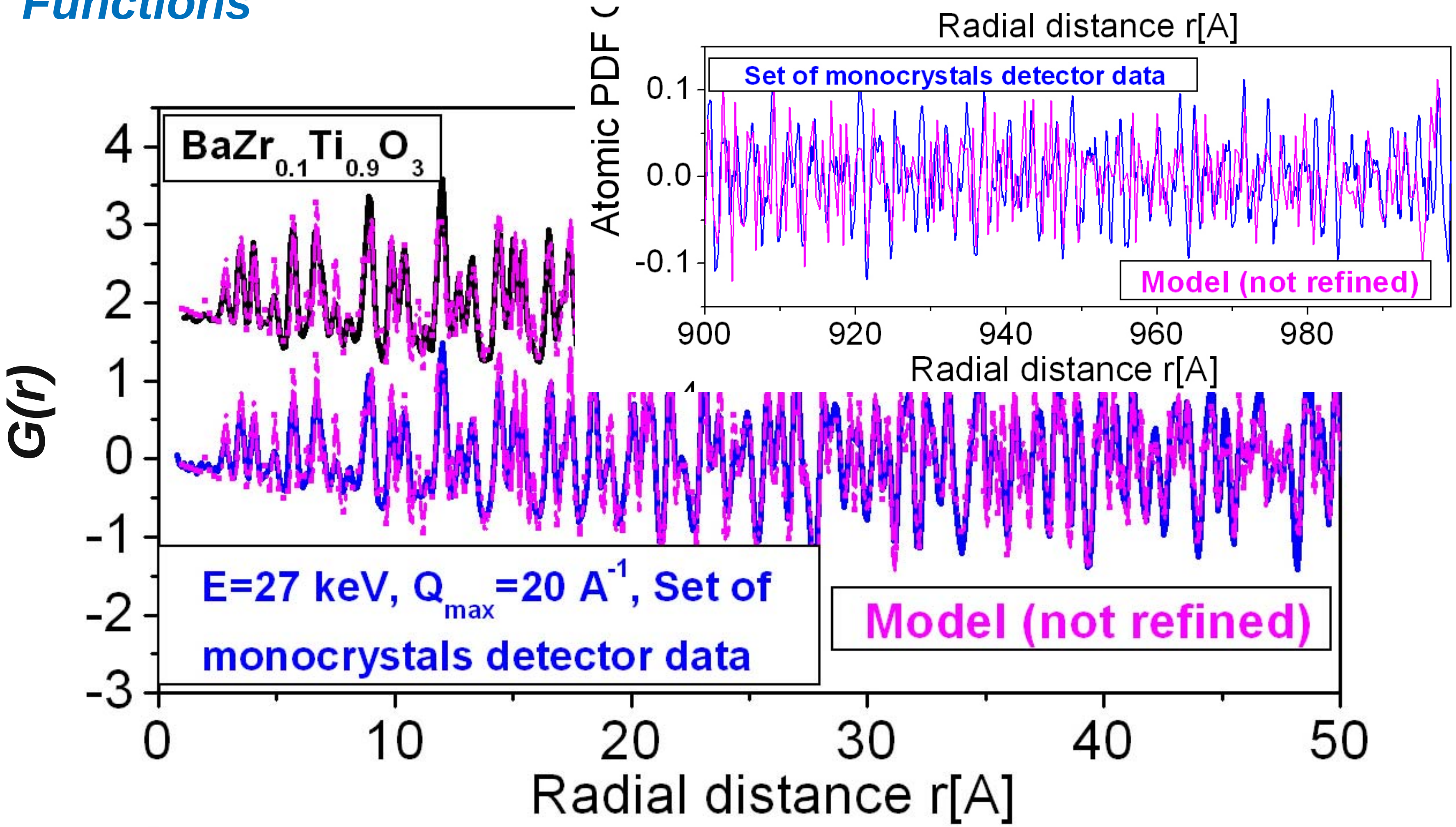
Coming soon:

- Wider temperature range for on-site work: soon up to 1000 C, later down to ~10 K. (Note: 90 K – 500 K for mail-in)
- Facile wavelength changes for resonant scattering
- Area detection data collection systems
- Enhanced data security for proprietary measurements – need some help from this community



http://11bm.xor.aps.anl.gov

High-resolution Powder Diffraction and Pair-Distribution Functions



Courtesy of Valeri Petkov,
Central Michigan Univ.

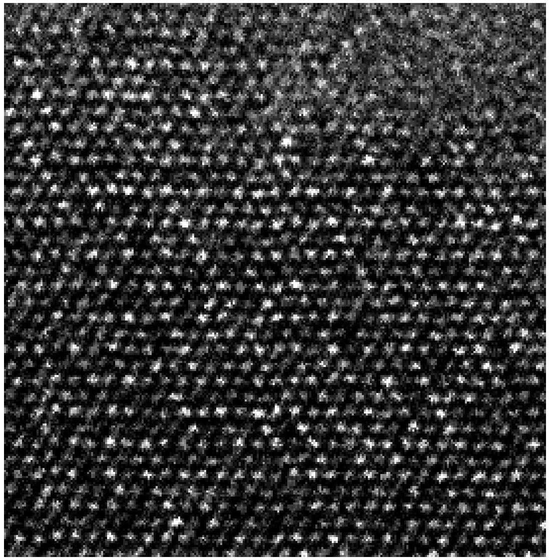
What can be done with high-resolution powder diffraction?

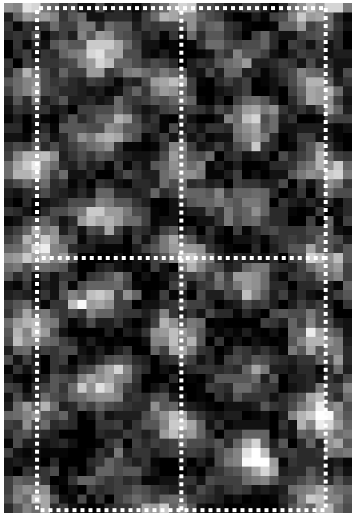
Propane Amoxidation: a decade+ mystery unraveled

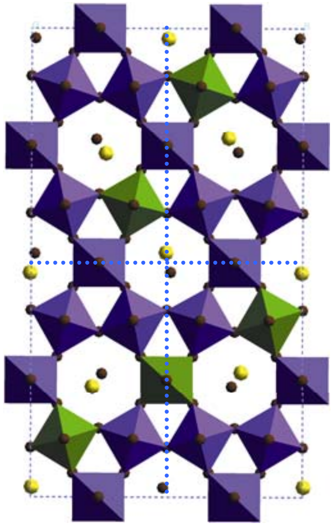
Poorly understood, but commercially very important catalyst mixture, even ~10 years after discovery

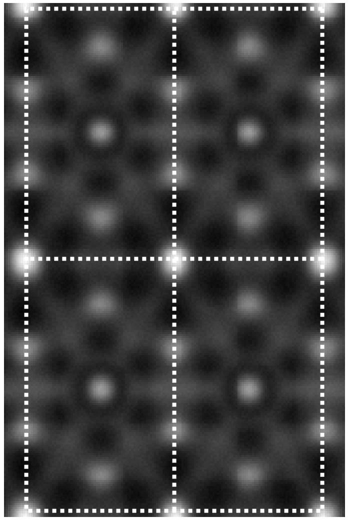
Breakthrough by group of Doug Buttrey (U. of DE) *et al.* by applying best-in-world research tools:

- Combinatorial synthesis: enhanced concentration of each phase (Symex)
- Atomic imaging by TEM
- High resolution X-ray powder diffraction (X7A @ BNL) allowed indexing of unit cells (correctly)





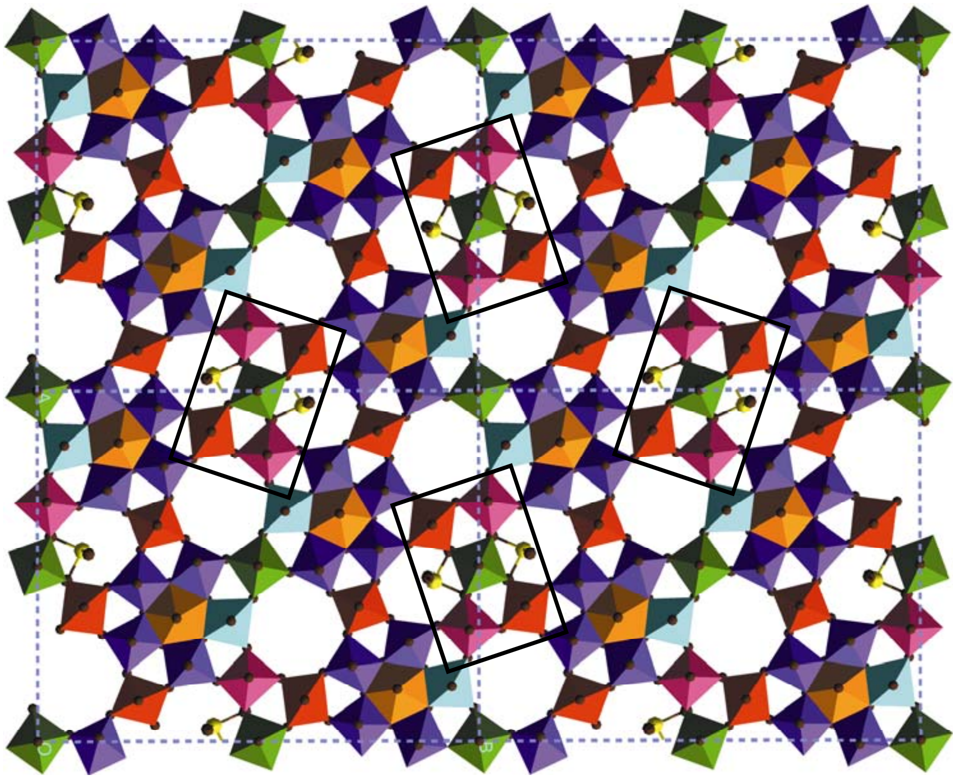




Armed with world-class tools, the structure & function could be explored

Crystallographic analysis:

- X-ray: metal sites
- Neutron: oxygen sites
- Combined fit:
  - Accurate M-O distances
  - Allows assigment of metal siting and <u>*valences*</u>
- Full structure: 16 metal sites (Mo,V,Te,Nb), 30 O atoms



Based on this detailed structure, a formal catalysis mechanism was proposed!

P. DeSanto Jr, D. J. Buttrey, R. K. Grasselli, C. G. Lugmair, A. F. Volpe Jr., B. H. Toby, & T. Vogt, *Topics in Catalysis*, 2003.

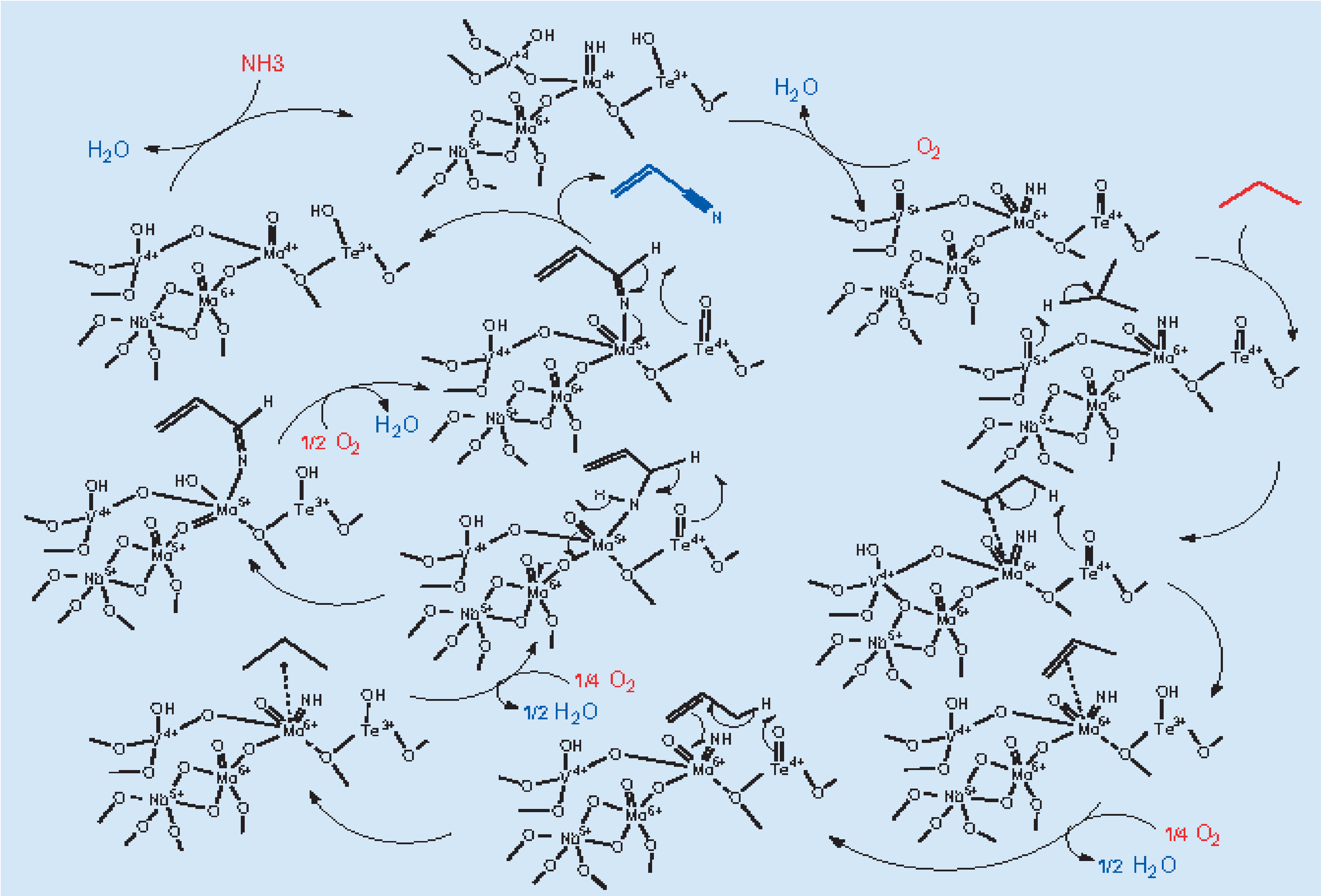


Fig. 2. A schematic mechanism for propane ammoxidation by the M1 catalyst that details the cation centers believed to be responsible for reactive process [3].

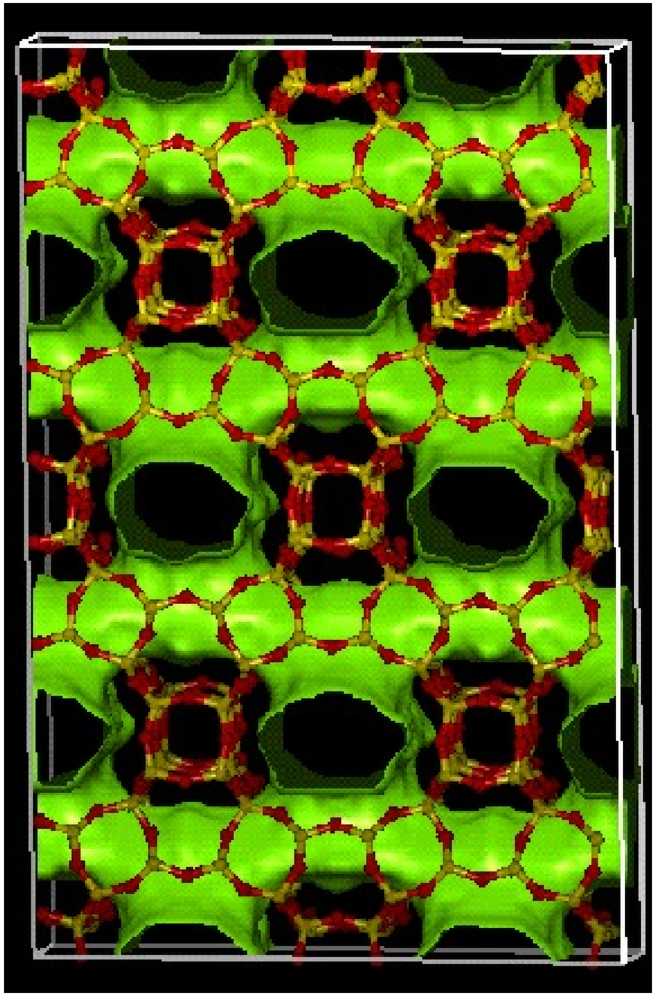
Powder Diffraction: Principle research tool for Zeolitic Materials

- Zeolites are **porous** aluminosilicate minerals *[naturally occurring]*
- ...built from tetrahedral SiO_4 and AlO_4 units
- Charge balance requires extra-framework cations:

$$\boldsymbol{M}^{+n}_{x/n}\,(AlO_2)^{-}_{x}\,(SiO_2)_{1-x}$$

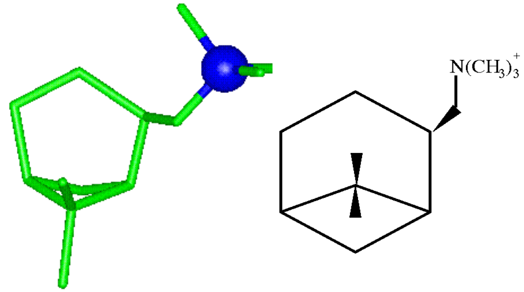
Many other framework atoms can be used to create *zeolitic* materials

Used for catalysis, selective adsorption, ion exchange…



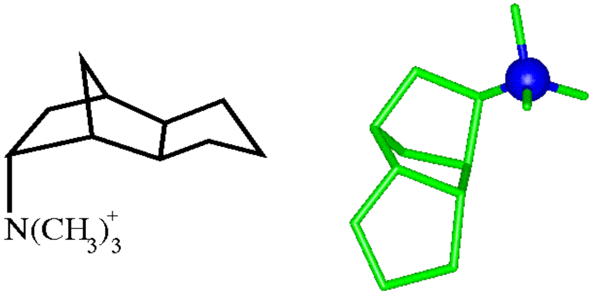
CIT-1: Unraveling how zeolites form

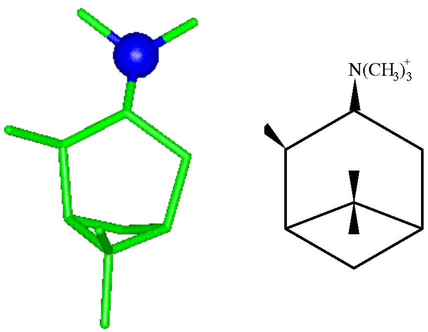
Many zeolitic materials are synthesized using organic “structure directing agent” (SDA) cations. This example illustrates how structural analysis validates modeling and explains the nature of zeolite-SDA interactions and how they drive synthesis.



◀ **1** Makes CIT-1 (~1% stacking faults)

2 Makes SSZ-33 (similar to CIT-1, but with >30% stacking faults) ▶



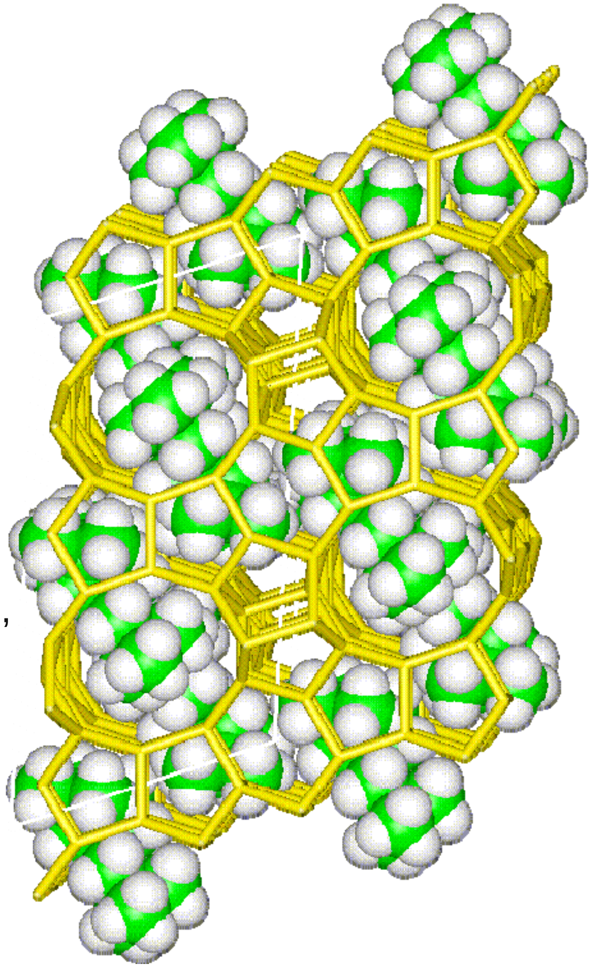


◀ **3** Cannot be used to make either CIT-1 or SSZ-33

There are no obvious differences.
Research problem: Why do the cations behave differently?

CIT-1: Conclusions

- Use of combined synchrotron and neutron diffraction gave cation siting: contradicts Monte-Carlo “docking” results
- Confirmed as unique solution by molecular modeling
- Explained why SDA **3** does not make CIT-1
- Stacking faults likely a kinetic phenomenon



Toby, Brian H., Khosrovani, Nazy, Dartt, Christopher B., Davis, Mark E., and Parise, John B., "Structure-directing Agents and Stacking Faults in the CON System: A Combined Crystallographic and Computer Simulation Study.", ***Microporous and Mesoporous Materials*** 39, 77 (2000).