IUCr-2021

18 August 2021

In the age of electrons, do we still need powder diffraction?

Stef Smeets

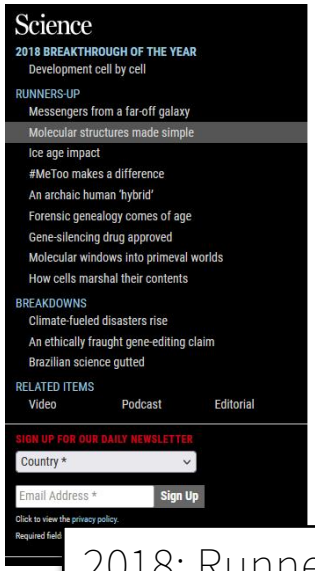
s.smeets@esciencecenter.nl

netherlands eScience center

Lukáš Palatinus

ECM-31 (Oviedo, 23-08-2018)

Crystallography in the 21st Century, the age of electrons?


Science

2018 BREAKTHROUGH OF THE YEAR
Development cell by cell

RUNNERS-UP
Messengers from a far-off galaxy
Molecular structures made simple
Ice age impact
#MeToo makes a difference
An archaic human 'hybrid'
Forensic genealogy comes of age
Gene-silencing drug approved
Molecular windows into primeval worlds
How cells marshal their contents

BREAKDOWNS
Climate-fueled disasters rise
An ethically fraught gene-editing claim
Brazilian science gutted

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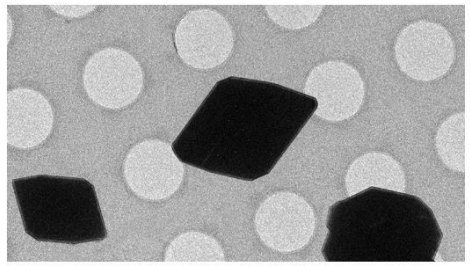


Molecular structures made simple

Structures can now be gleaned from micrometer-size crystals (black), seen here on an electron microscope slide. (GONEN LAB)

Two research teams simultaneously published papers in October revealing a new way to determine the molecular structures of small organic compounds in just minutes, rather than the days, weeks, or months required by traditional methods.

For decades, the gold standard for molecular mapping has been a technique known as x-ray crystallography, which involves firing a beam of x-rays at a crystal containing millions of copies of a molecule lined up in a common orientation. Researchers then track the way x-rays bounce off

2018: Runner-up breakthrough of the year

2019: The revolution

ACS central science

Outlook

Cite This: *ACS Cent. Sci.* 2019, 5, 1315−1329

http://pubs.acs.org/journal/acscii

3D Electron Diffraction: The Nanocrystallography Revolution

Mauro Gemmi,*,† Enrico Mugnaioli,† Tatiana E. Gorelik,‡ Ute Kolb,§,∥ Lukas Palatinus,⊥ Philippe Boullay,# Sven Hovmöller,∇ and Jan Pieter Abrahams○,◆,¶

2021: Dedicated equipment

Also 2019:

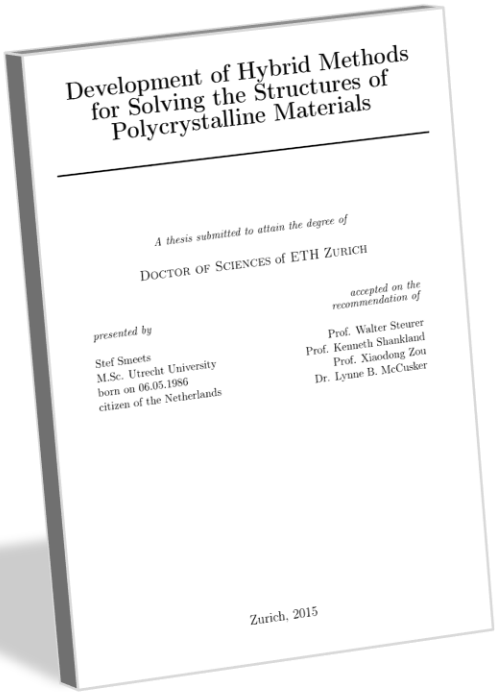
ABSTRACTS

Acta Cryst. (2019). A**75**, a261

The death of powder – micro-electron diffraction with EIGER

C. Schulze-Briese, A. Förster, P. Hofer, S. De Carlo, L. Piazza, J. T. C. Wennmacher and T. Grüne

In the not so distant past…


Development of Hybrid Methods for Solving the Structures of Polycrystalline Materials

A thesis submitted to attain the degree of

DOCTOR OF SCIENCES of ETH ZURICH

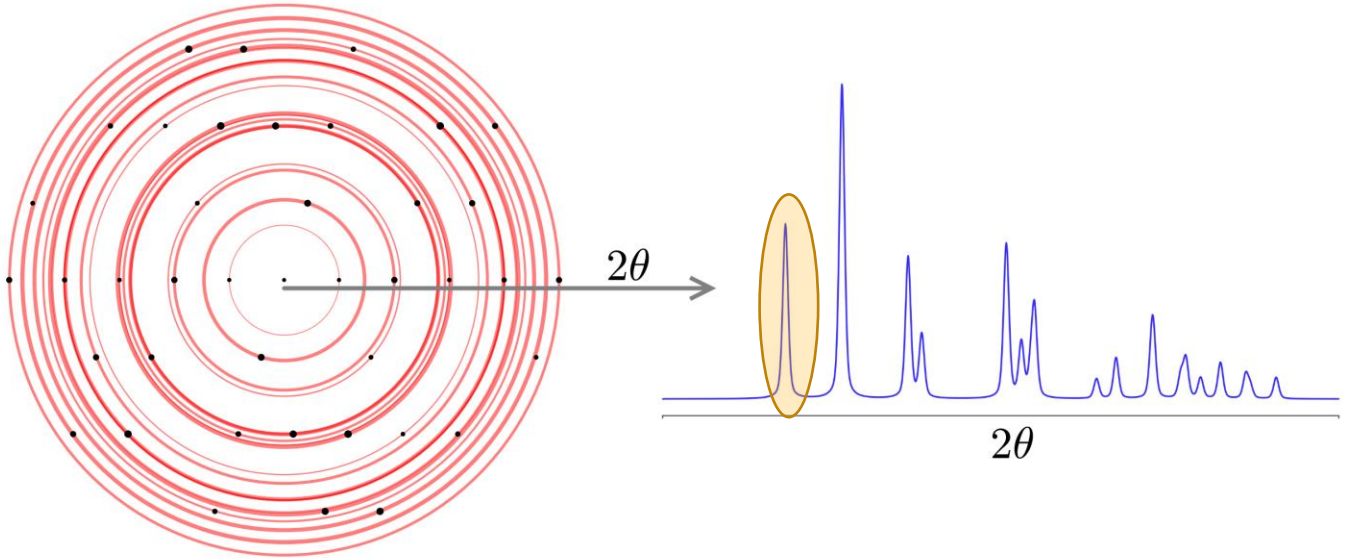
presented by

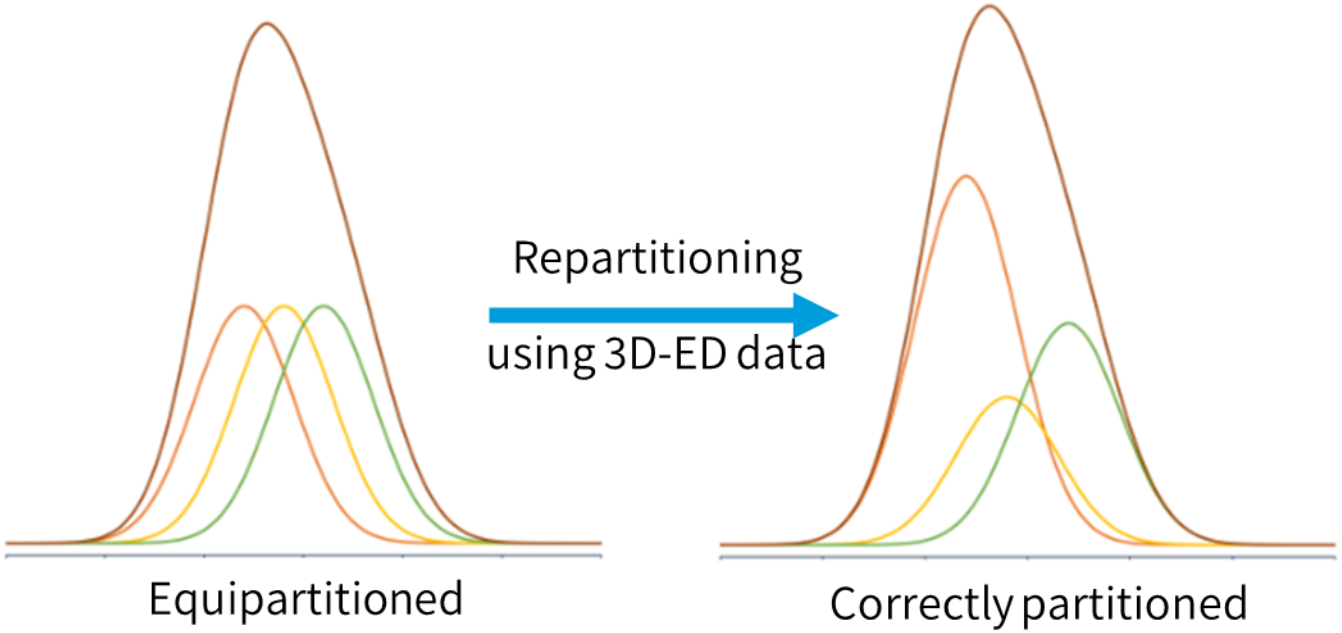
Stef Smeets
M.Sc. Utrecht University
born on 06.05.1986
citizen of the Netherlands

accepted on the recommendation of

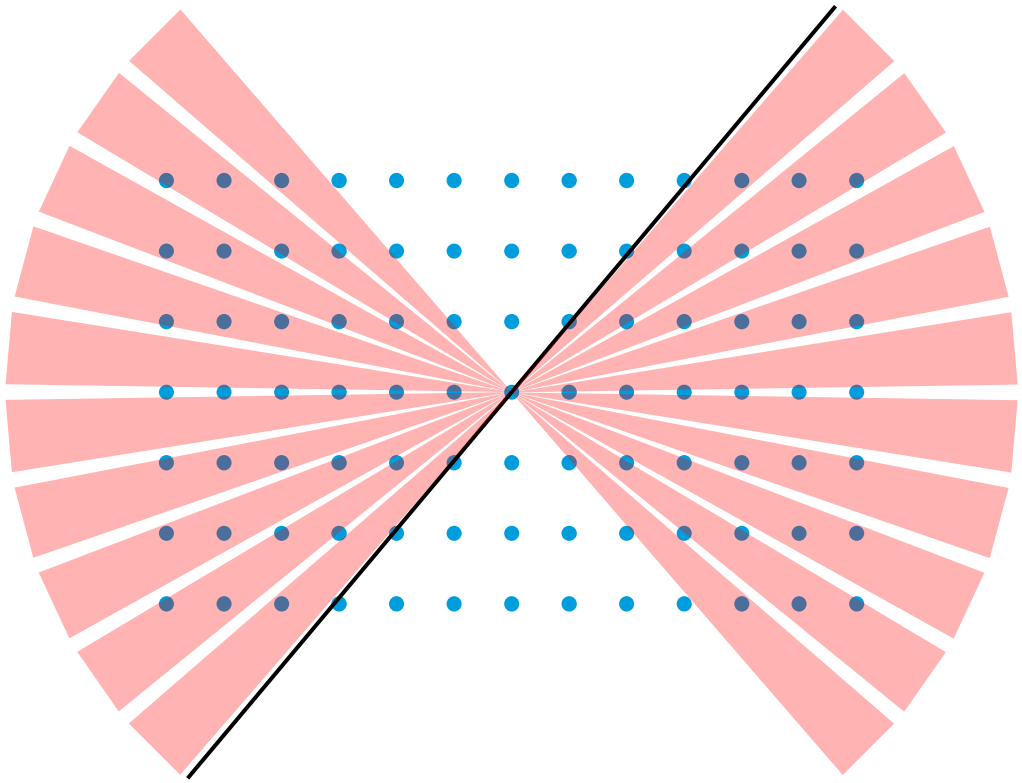
Prof. Walter Steurer
Prof. Kenneth Shankland
Prof. Xiaodong Zou
Dr. Lynne B. McCusker

Zurich, 2015



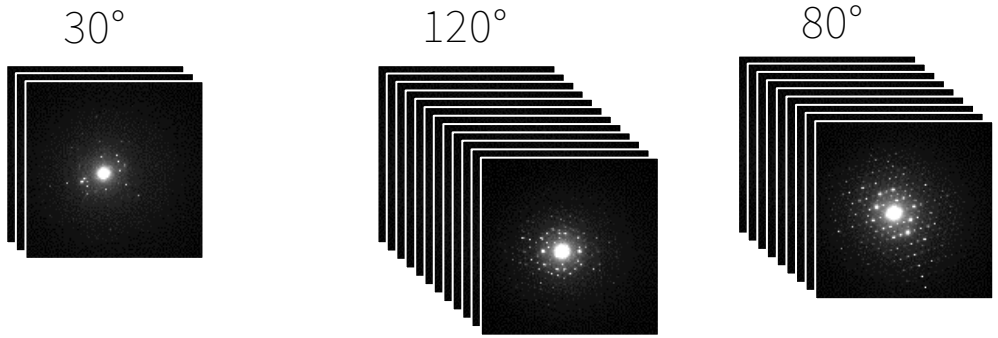


Typical workflow

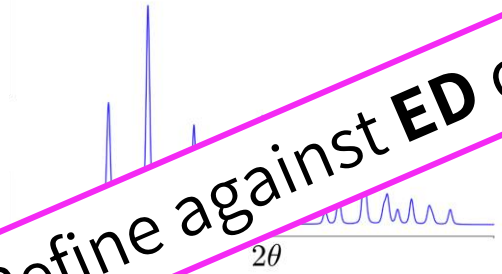


3D-ED / microED
Data collection

1. Collect ED data on a few crystals



2. Solve with SHELXS/SHELXT/Superflip/SIR



3. Refine against **ED** data

3. Refine against XRPD data

In the age of electrons, do we still need powder diffraction?

- SSZ-27 – What if our crystal selection is biased?
- SerialED – Can we do quantitative phase analysis using ED?
- SerialRED – Can we do phase identification using ED?

Zeolite SSZ-27

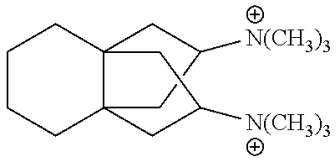
What if our crystal selection is biased?

Zeolite SSZ-27

Synthesis

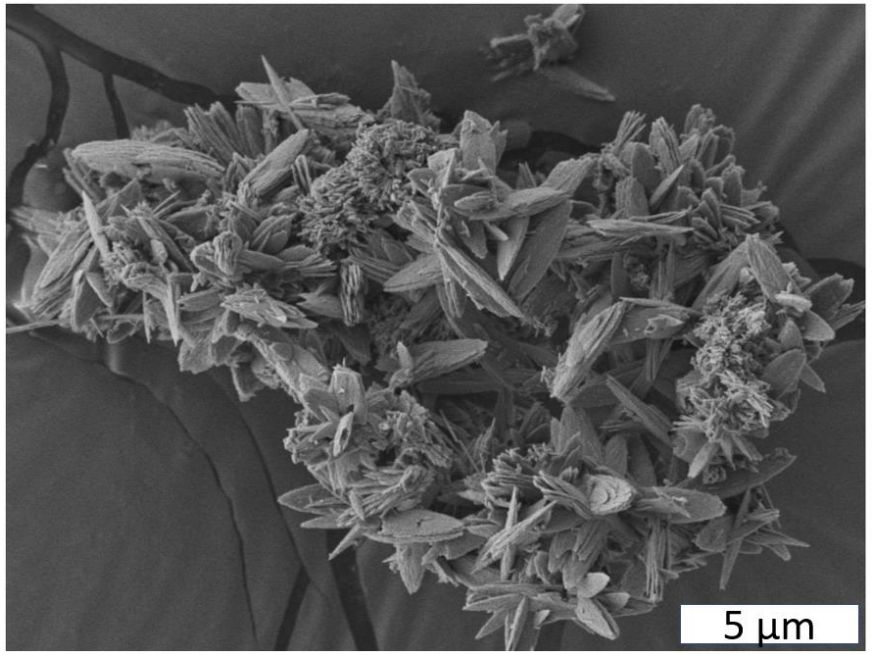
S.I. Zones, D. Xie, and R.J. Saxton, US patent 9,586,829 B2 (2017)
Molecular sieve SSZ-27

Aluminosilicate, Si:Al = ~14



hexamethyl [4.3.3.0] propellane-8, 11-diammonium cation

Organic template



Microcrystalline powder

Applications

- Adsorbent for gas separation
- Catalyst MTO/amine synthesis
- DeNOx
- Hydrocarbon trap (C_3)

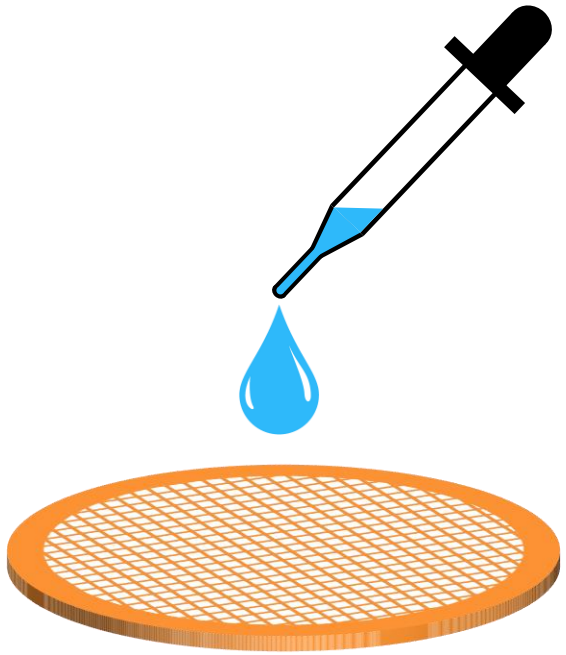
Electron diffraction data collection

Pick a single crystal for data collection

150 µm

Sample prep

Crystalline powder
(Disperse in EtOH)



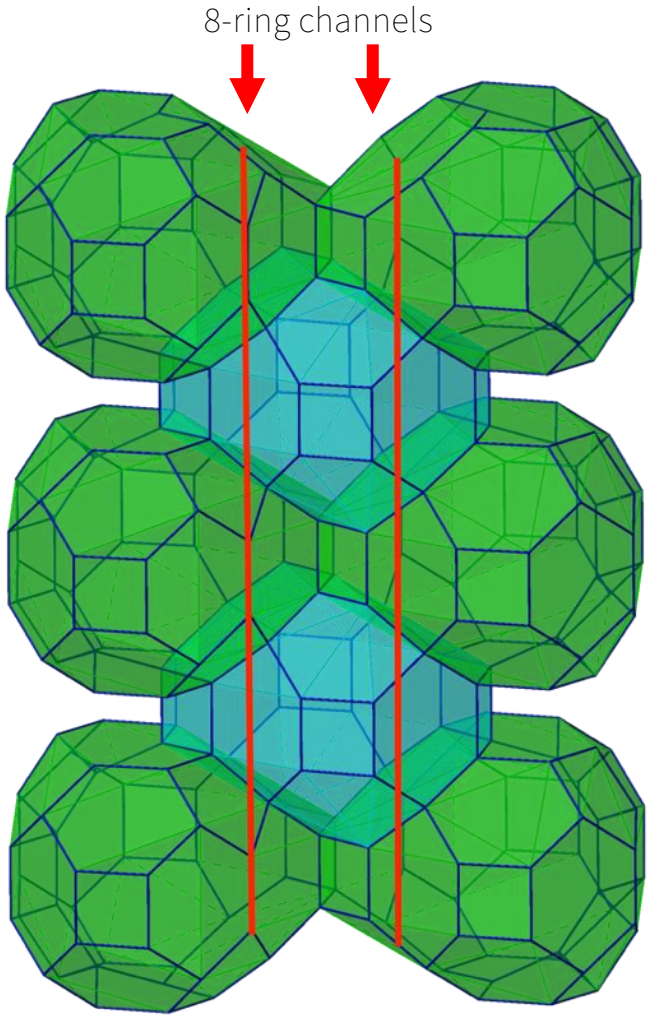
3 mm Cu grid

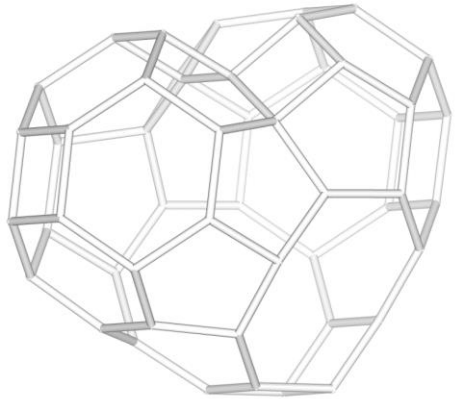
Structure analysis

3D electron diffraction
Collected by Lukas Palatinus (2012)

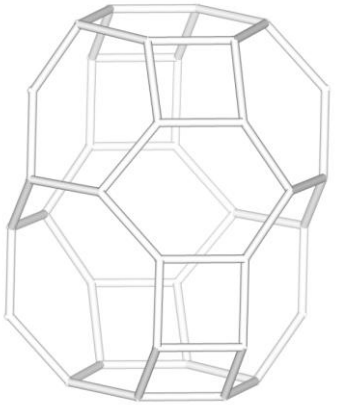
$C2/m$
$a = 23.95$ Å
$b = 13.79$ Å
$c = 24.96$ Å
$\beta = 115.7°$

Solved with Superflip and FOCUS





Two types of cavities



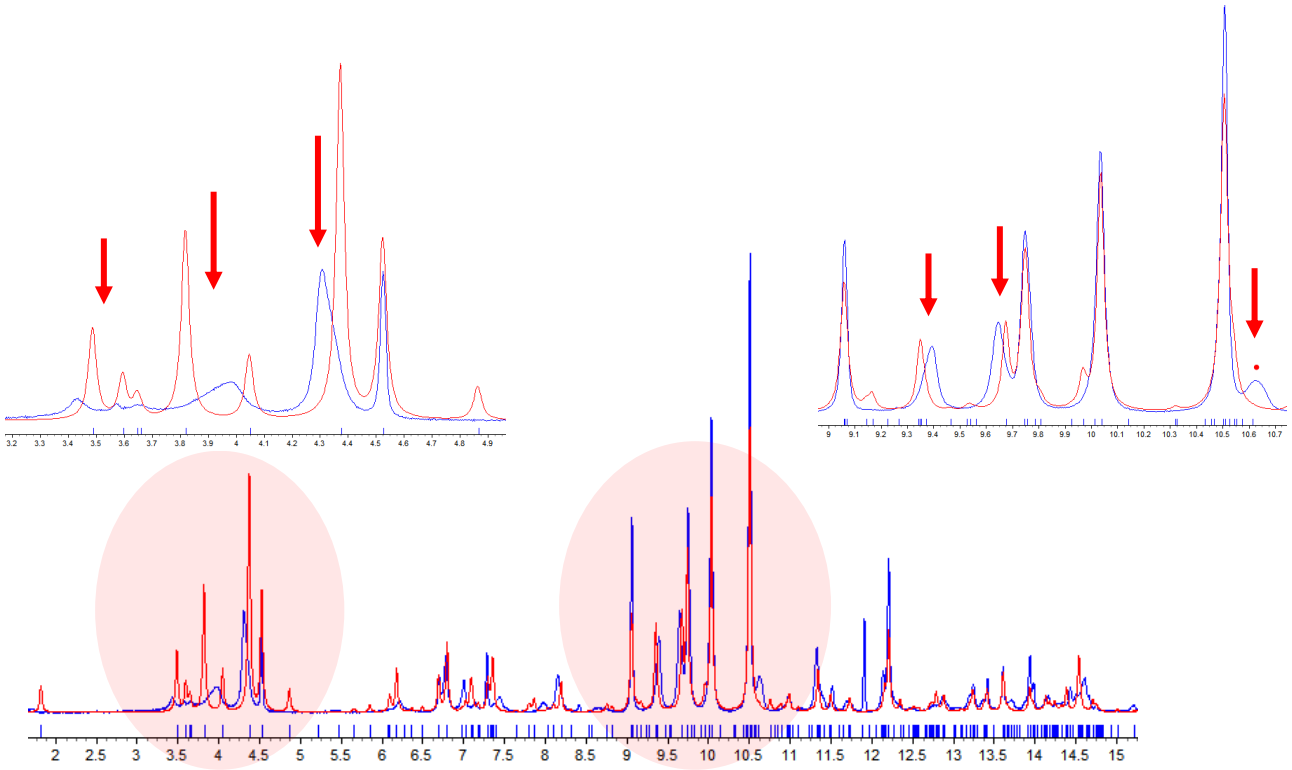
Structure did not match powder data

3D electron diffraction
Collected by Lukas Palatinus (2012)

$C2/m$
$a = 23.95$ Å
$b = 13.79$ Å
$c = 24.96$ Å
$\beta = 115.7°$

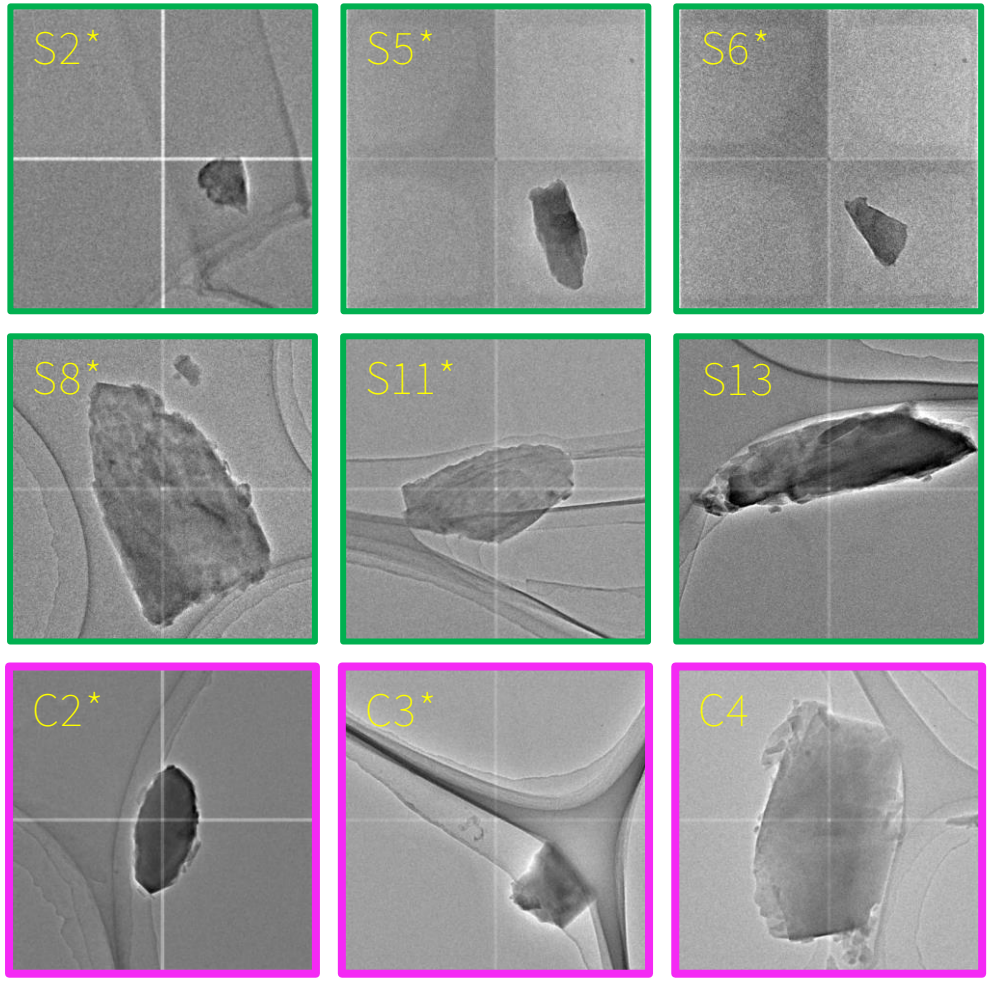
Solved with Superflip and FOCUS

Synchrotron X-ray powder diffraction
Profile refinement failed



Collect ED data on a few more crystals

Total: 18 crystals



Phase 1 (14 crystals)

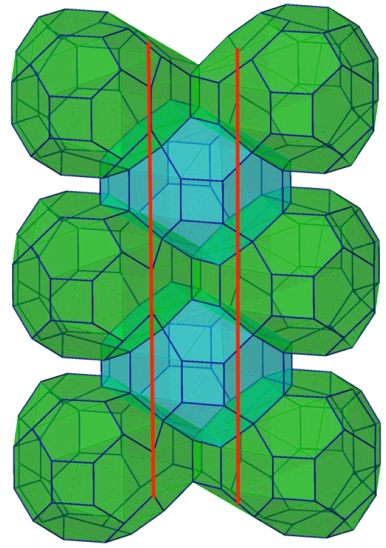
$C2/m$

$a = 24.12$ Å

$b = 13.81$ Å

$c = 25.07$ Å

$\beta = 115.19°$



New phase (SSZ-27)

Phase 2 (4 crystals)

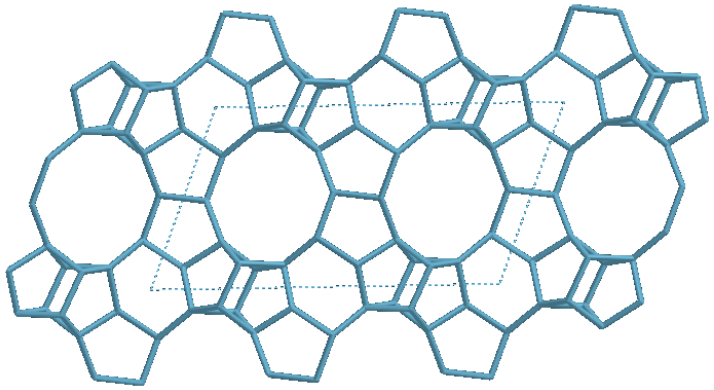
$C2/m$

$a = 23.40$ Å

$b = 13.77$ Å

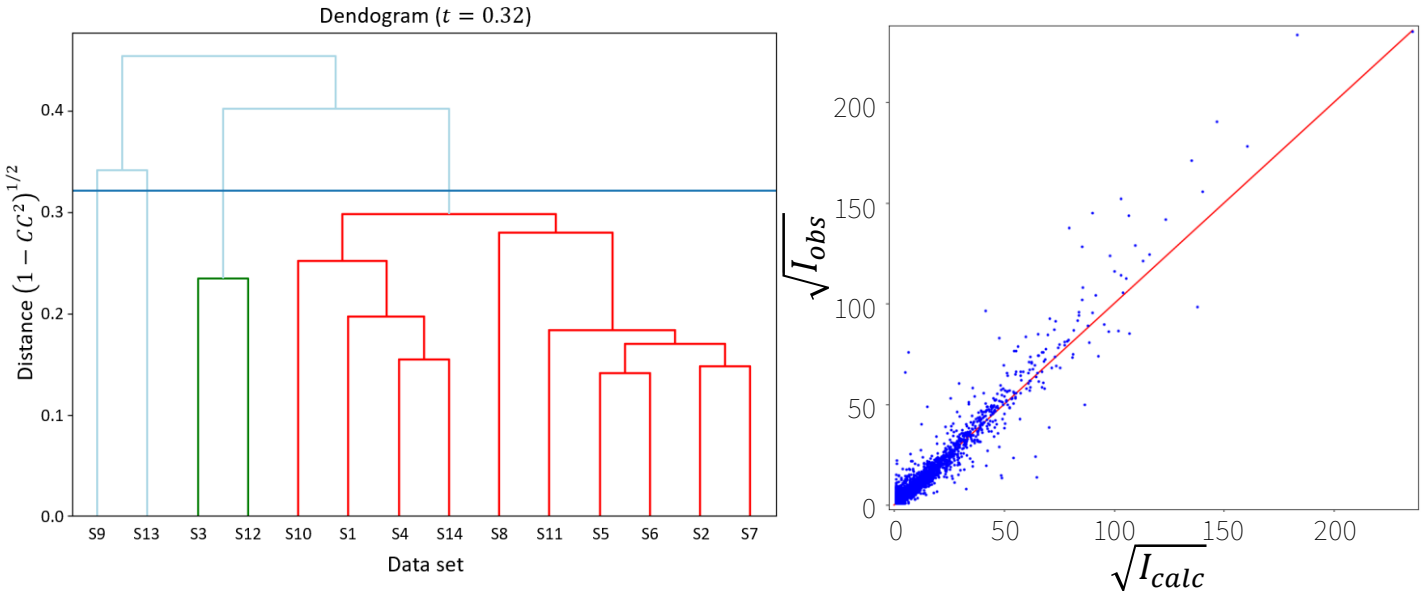
$c = 12.73$ Å

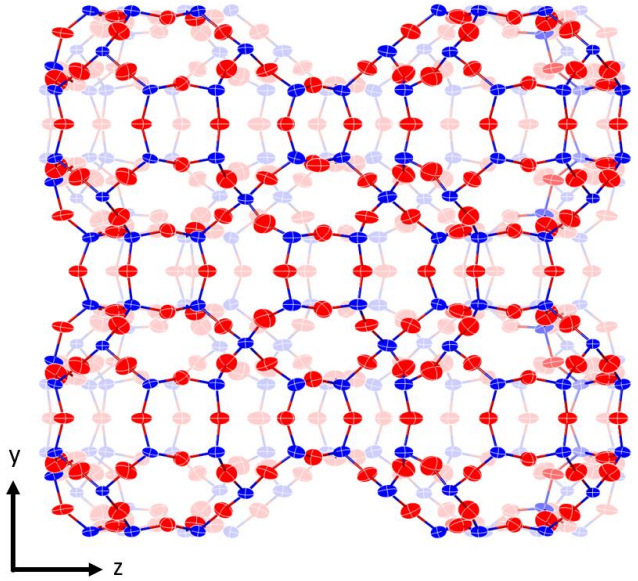
$\beta = 110.89°$

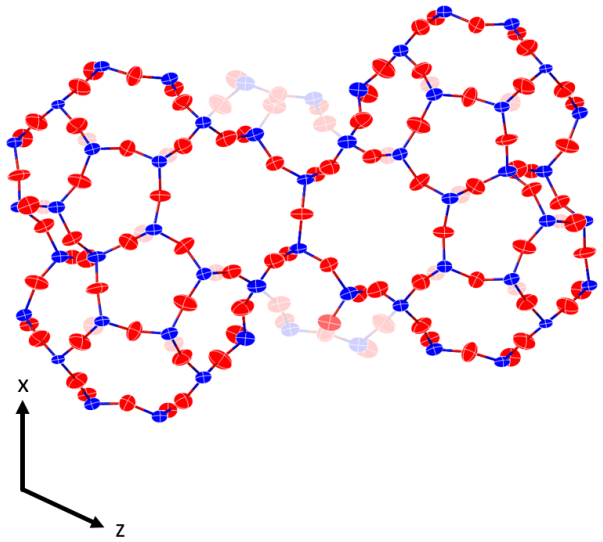


Known phase (CON)

SSZ-27 – Structure refinement (SHELXL)







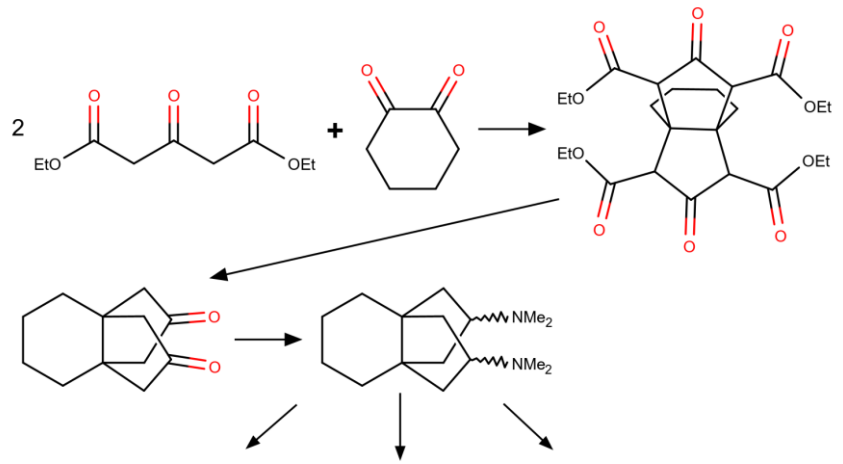
Combine 10 crystals for higher redundancy/completeness using hierarchical cluster analysis

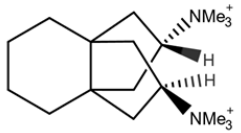
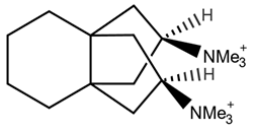
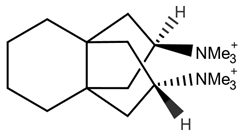
# Refs. (total)	130755	Completeness	98.8
# Refs. (unique)	7913	$CC_{1/2}$	98.8
# Refs. (obs.)	4129	R_{int}	0.287
Resolution (Å)	0.77	$R1$ [$\boldsymbol{I > 2\sigma(I)}$]	0.178

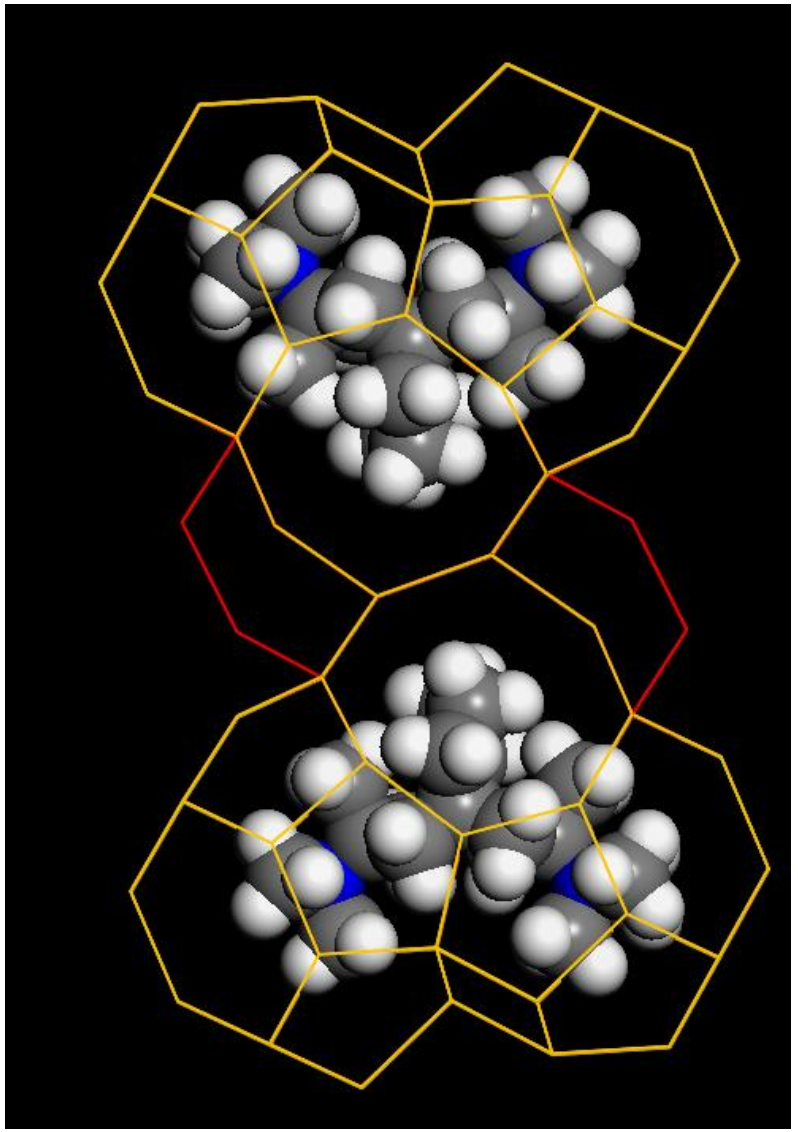
Smeets, *et al.*, *Angew. Chem. Int. Ed.* 58(37):13080, 2019

Molecular modelling confirms isomer specificity

Template synthesis forms
3 isomers

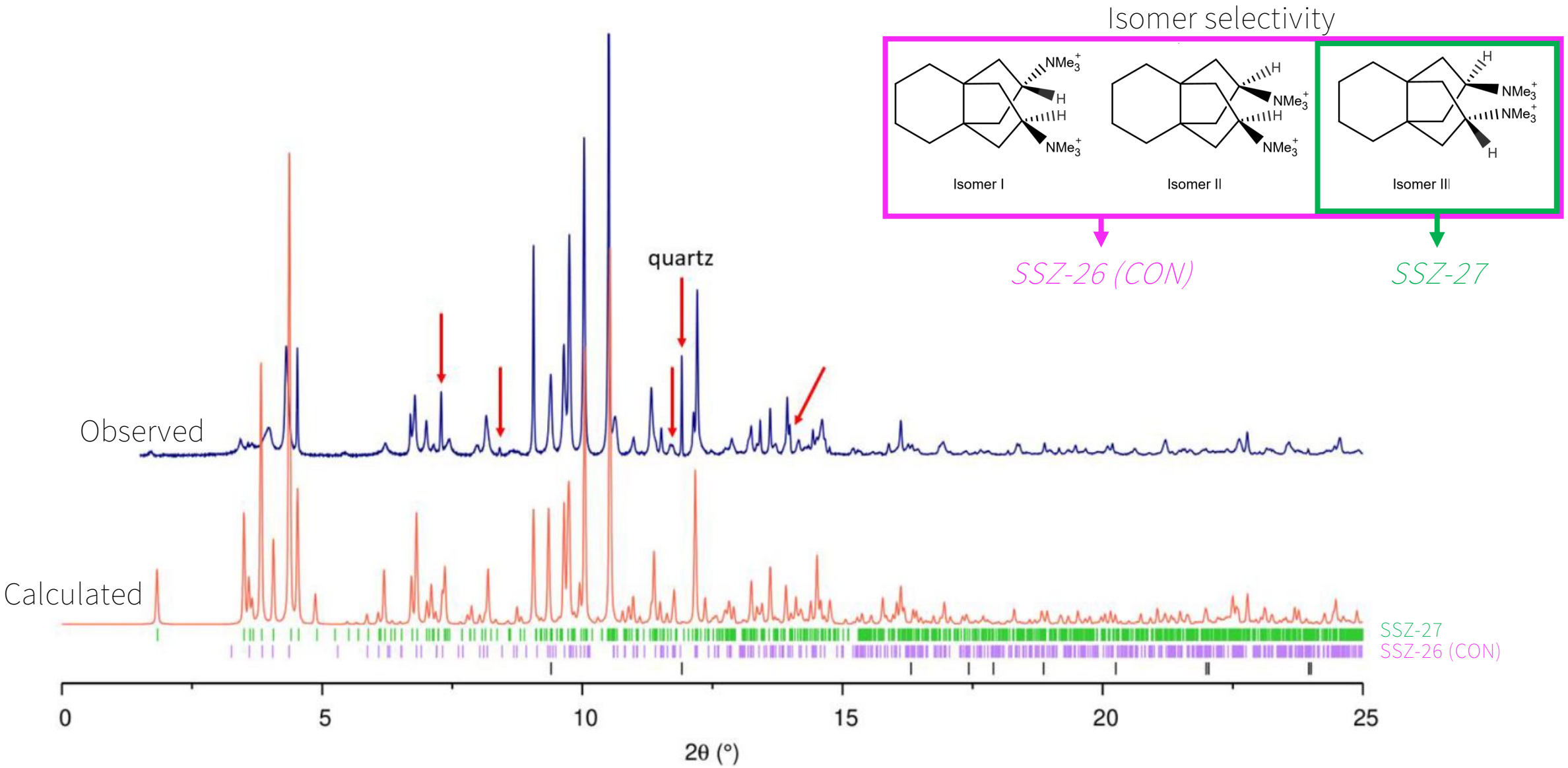


	Isomer I	Isomer II	Isomer III
			
SSZ-27 (kJ/mol Si)	-3.66	-3.31	-8.95
SSZ-26 (kJ/mol Si)	-7.60	-8.25	-8.18



Smeets, *et al.*, *Angew. Chem. Int. Ed.* 58(37):13080, 2019

Profile refinement against XRPD data



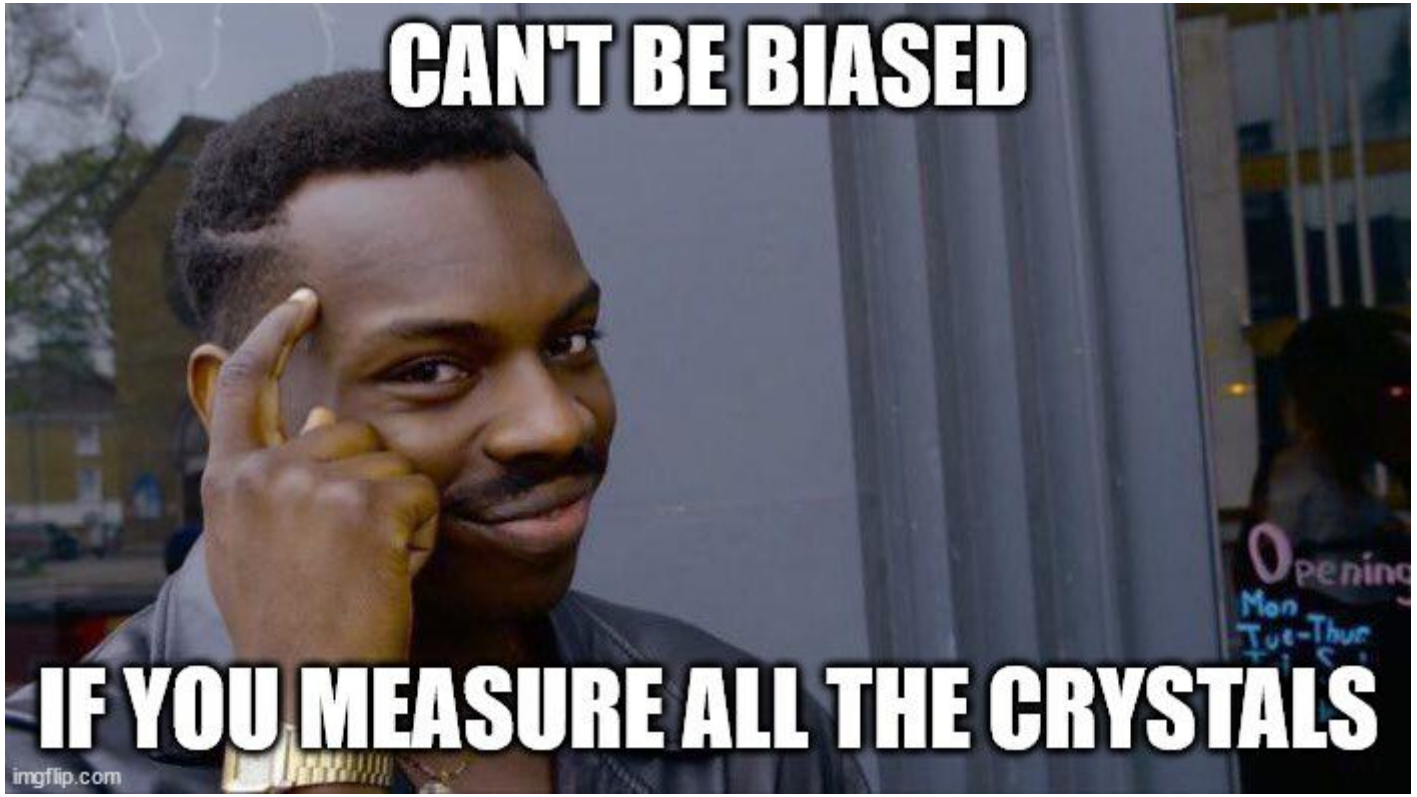
Summary SSZ-27

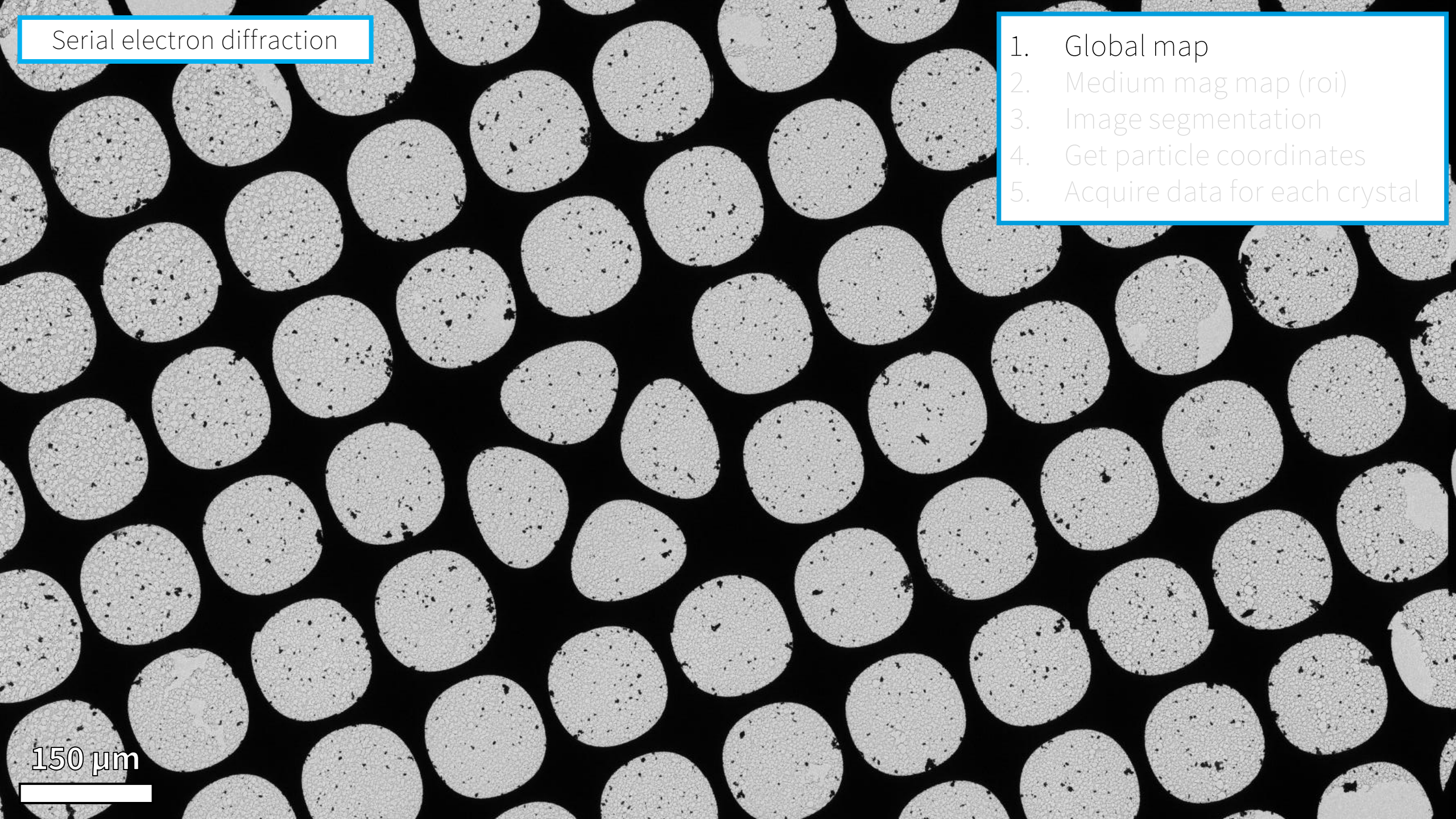
- 3D-ED data: crystal structure
- XPRD data: bulk structure

- ED data can be biased by crystal selection
- XRPD showed our model was not complete
- Combined data revealed new purification pathway

Serial electron diffraction

Can we do quantitative phase analysis using electron diffraction?

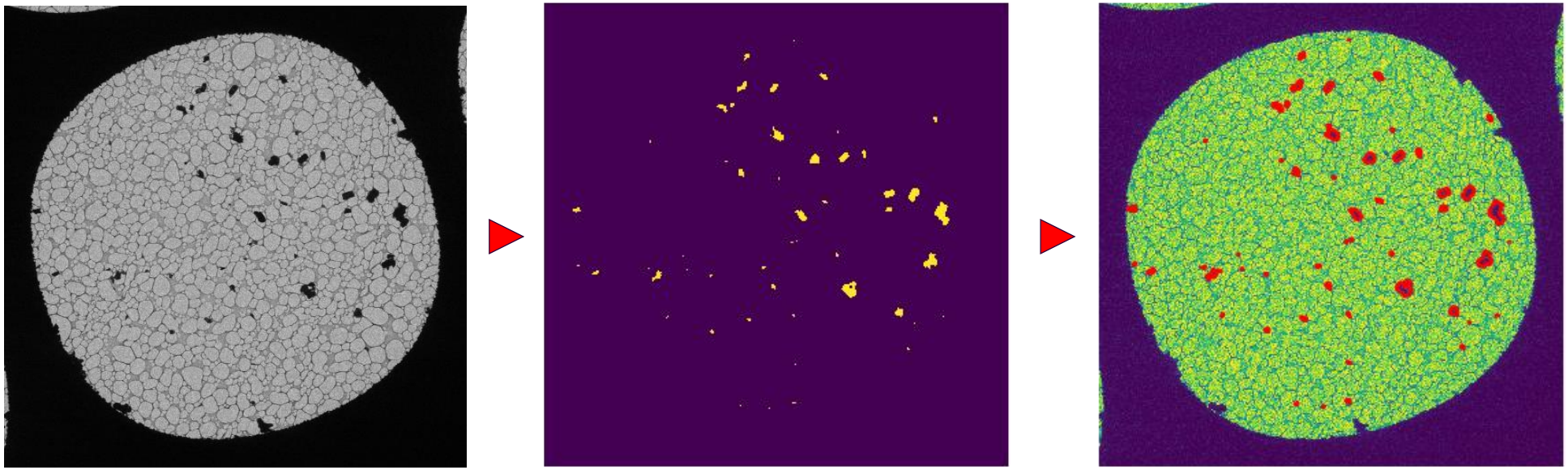



Serial electron diffraction
1. Global map
2. Medium mag map (roi)
3. Image segmentation
4. Get particle coordinates
5. Acquire data for each crystal
150 µm

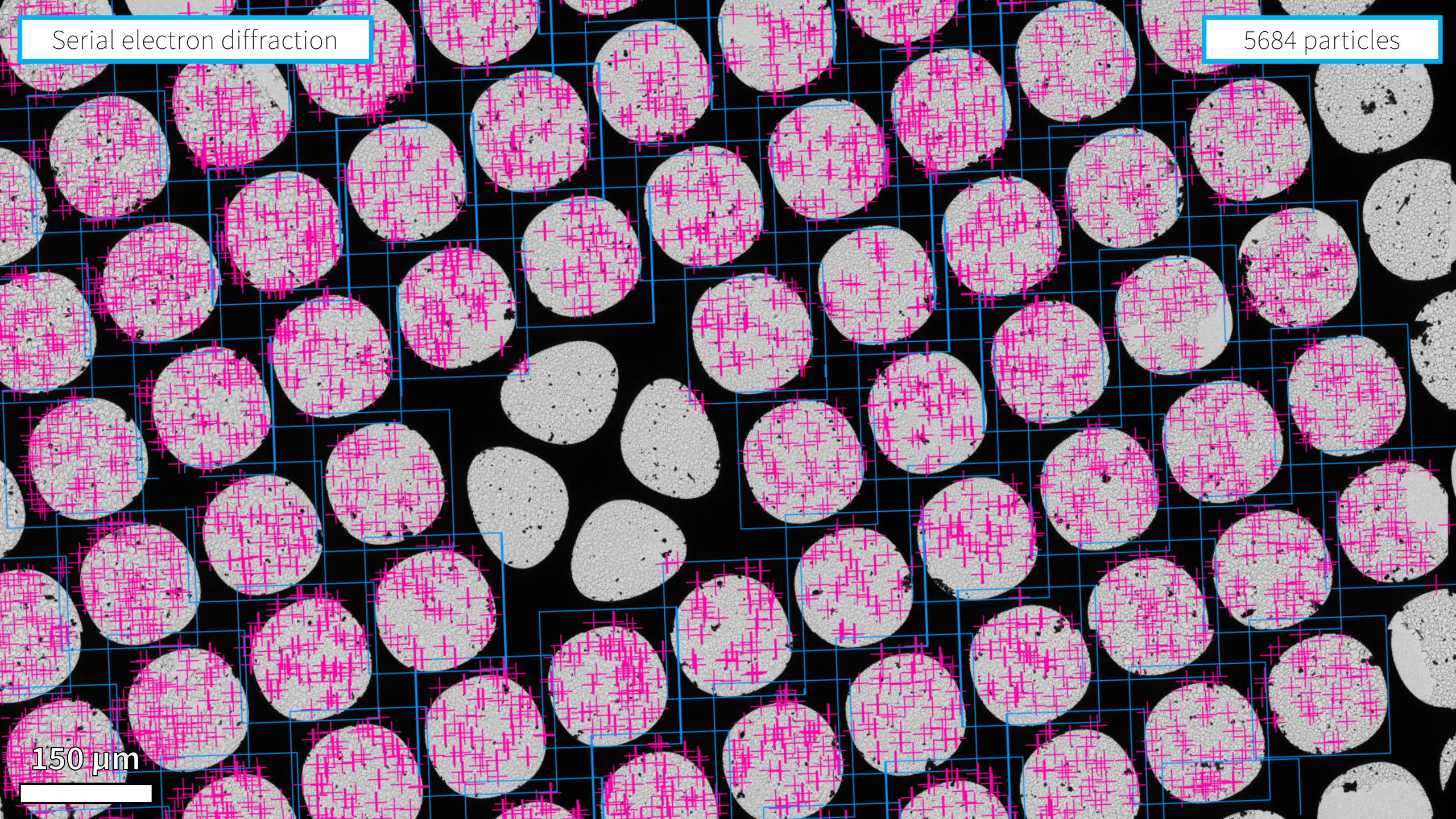

CRYSTALS
LIGHTYEAR
CRYSTALS EVERYWHERE
imgflip.com

Serial electron diffraction

1. Global map
2. Medium mag map (roi)
3. Image segmentation
4. Get particle coordinates
5. Acquire data for each crystal

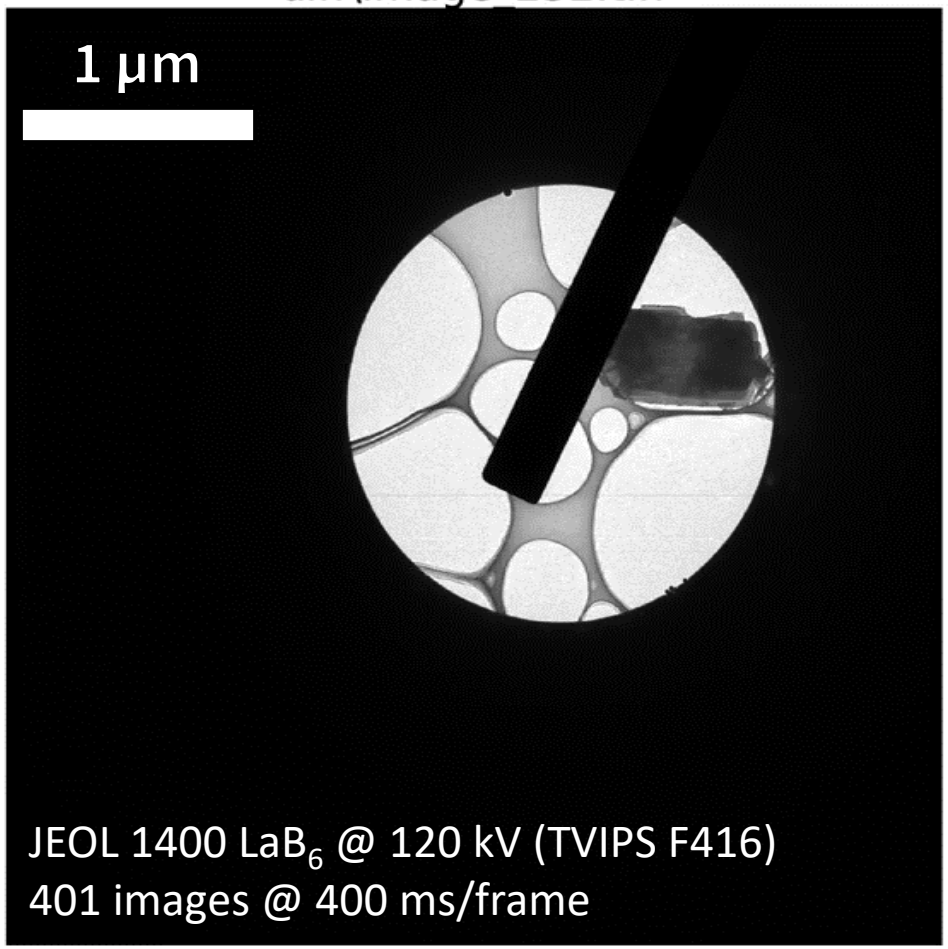


150 µm


Serial electron diffraction
5684 particles
150 µm

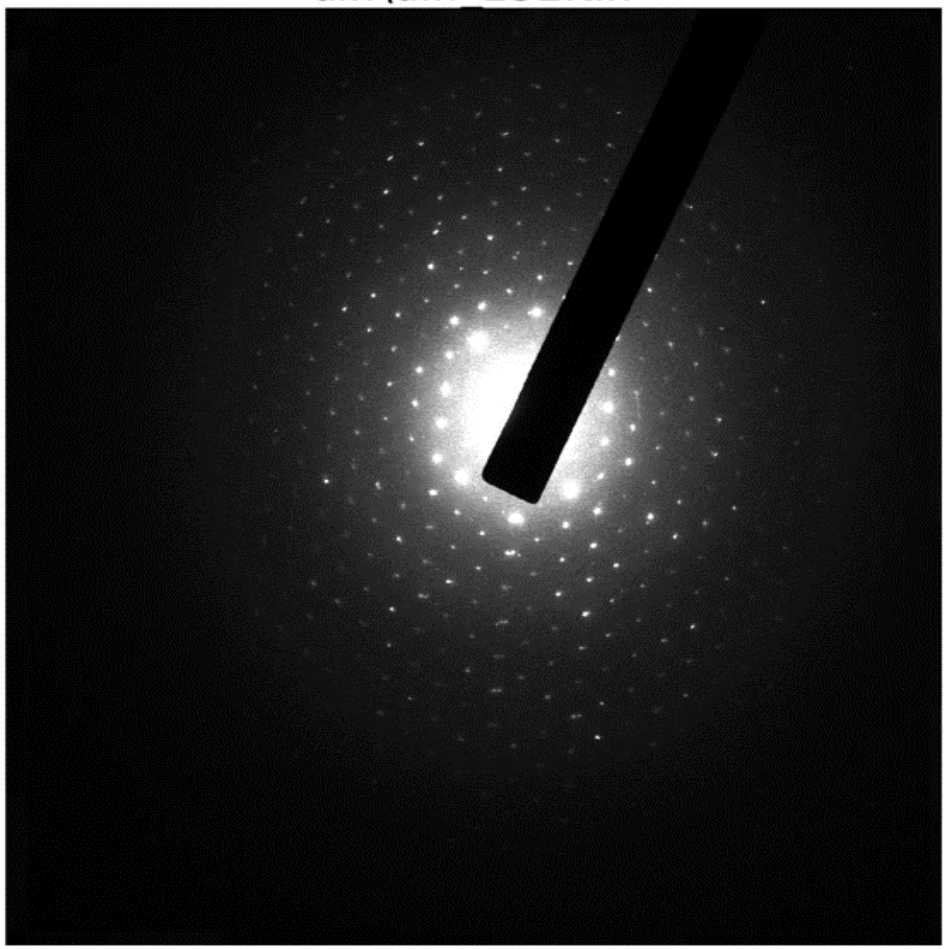
SerialED data collection (Zeolite)

diff\image_232.tiff



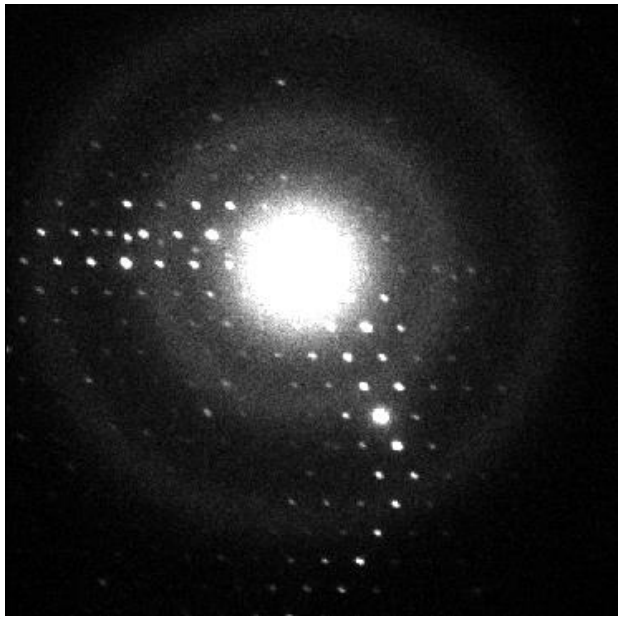
JEOL 1400 LaB_6 @ 120 kV (TVIPS F416)
401 images @ 400 ms/frame

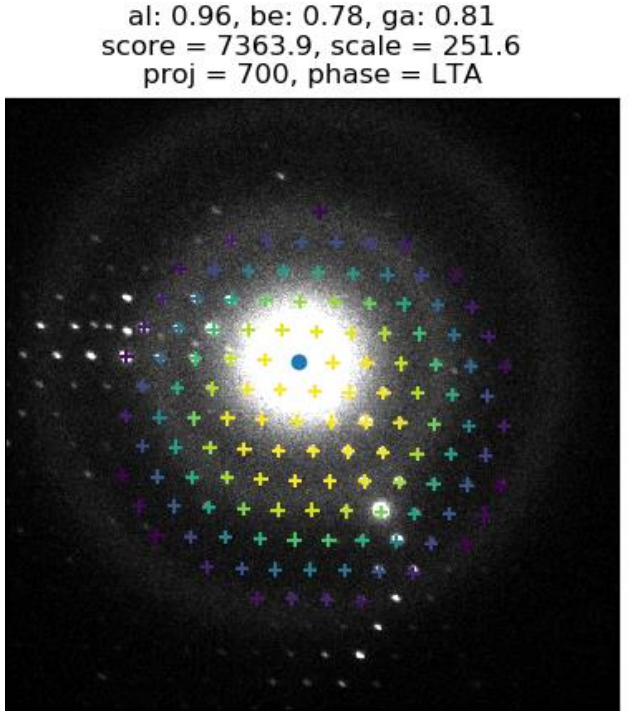
diff\diff_232.tiff

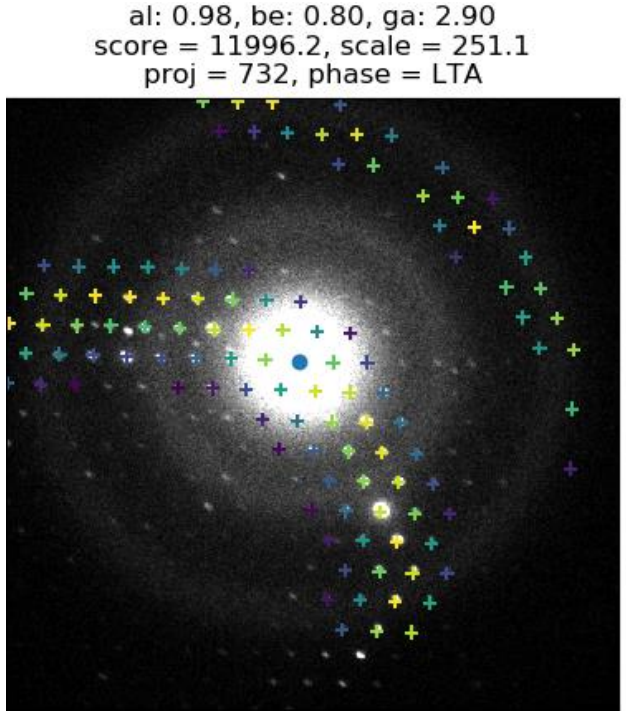


Indexing: orientation finding

- Forward projection model using known lattice parameters
- Generate pattern library of all possible orientations (~1.5M in $P1$)
- Match best orientation and index data







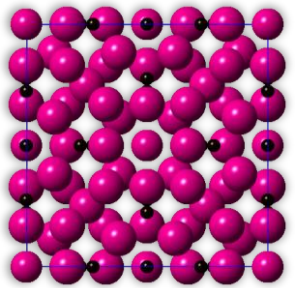
https://github.com/stefsmeets/problematic
Smeets *et al.*, *J. Appl. Cryst.*, 2018, 51:1262

Study on Cr Carbines

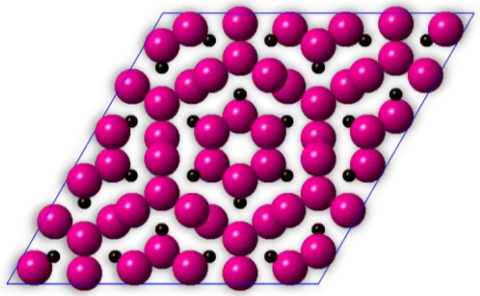
- Carbide: M_xC_y (M=Cr, Fe, Mo, …)
- Additive in steel manufacturing (≤ 5 wt%)
- Influences strength, ductility, corrosion resistance, etc

- Sample:
  - Phase isolates from martensitic stainless steel

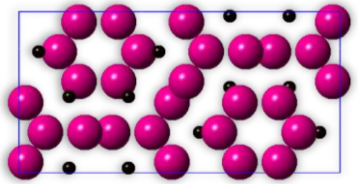
$M_{23}C_6$
$Fm\bar{3}m$
$a = 10.62$ Å



M_7C_3 (hex)
$P6_3mc$
$a = 13.77$ Å
$c = 4.88$ Å

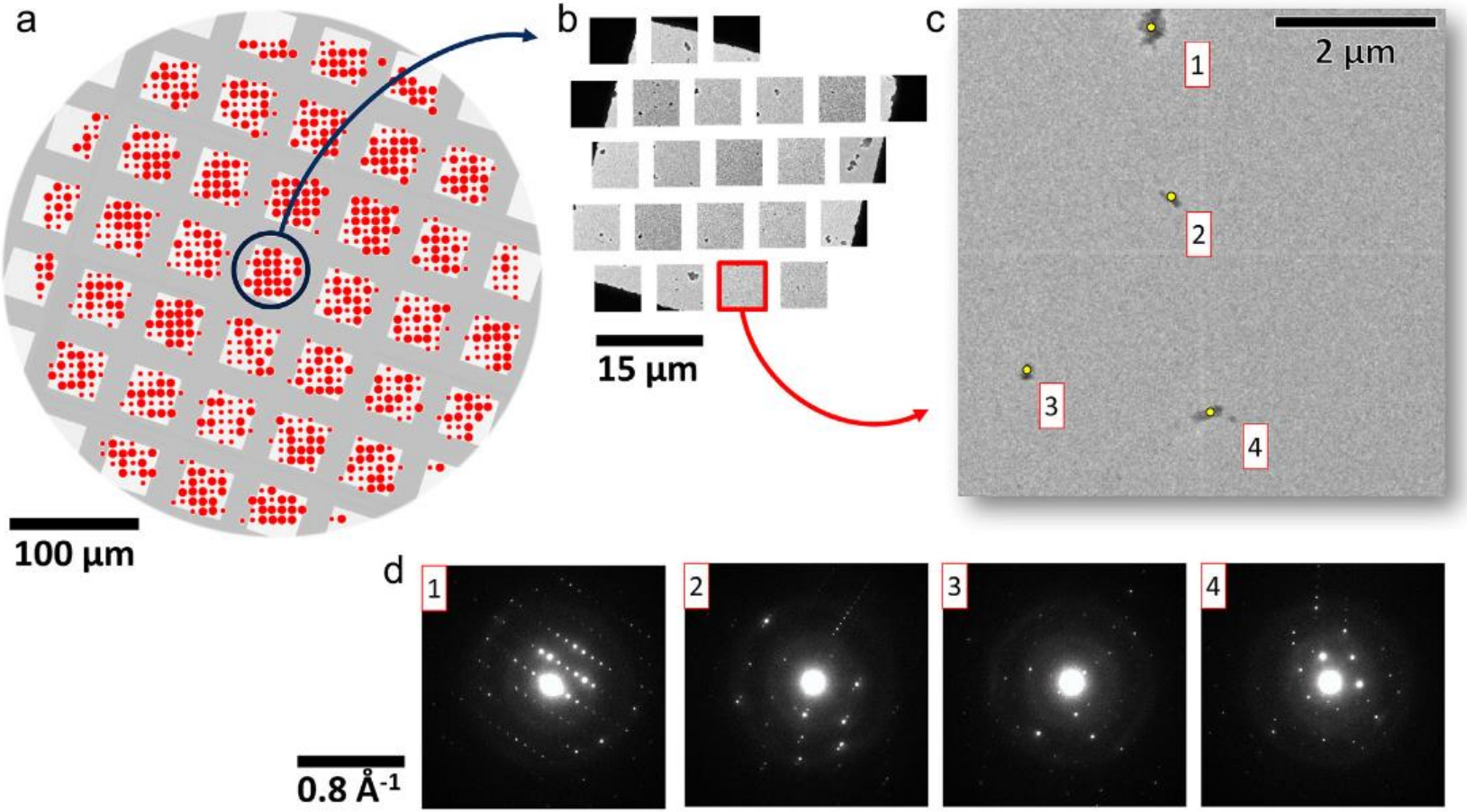


M_7C_3 (ortho)
$Pnma$
$a = 4.39$ Å
$b = 7.08$ Å
$c = 14.16$ Å



With Claes Olsson (Sandvik Materials Technology)
Smeets et al., *Steel Res. Int.* 90 (2019), 1800300

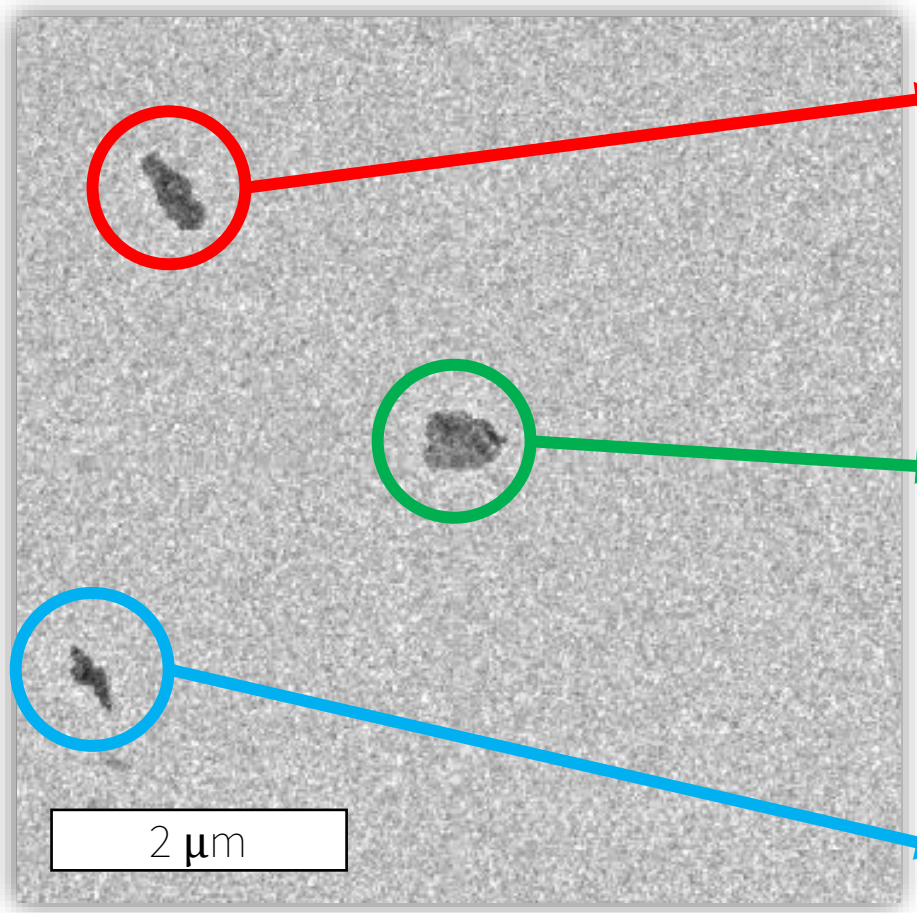
SerialED data collection

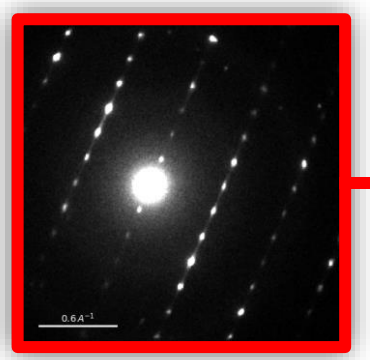


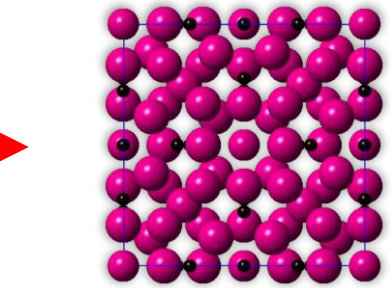
4 sessions
3939 particles
~4 hours total
1000 crystals/hr

Collected with Instamatic
JEOL 2100 with ASI Timepix

SerialED QPA

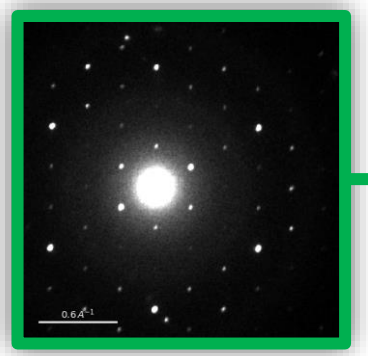


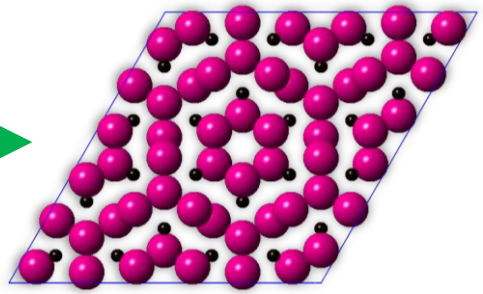




$M_{23}C_6$

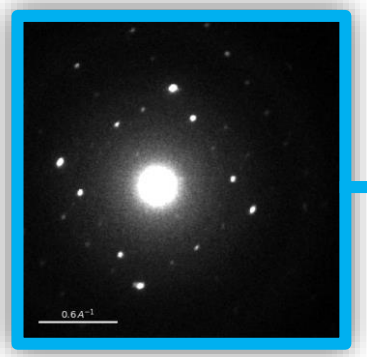
33.7%

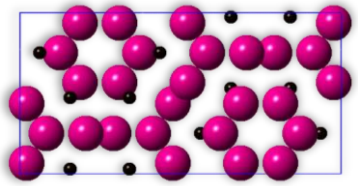




Cr_7C_3 (hex)

6.4%



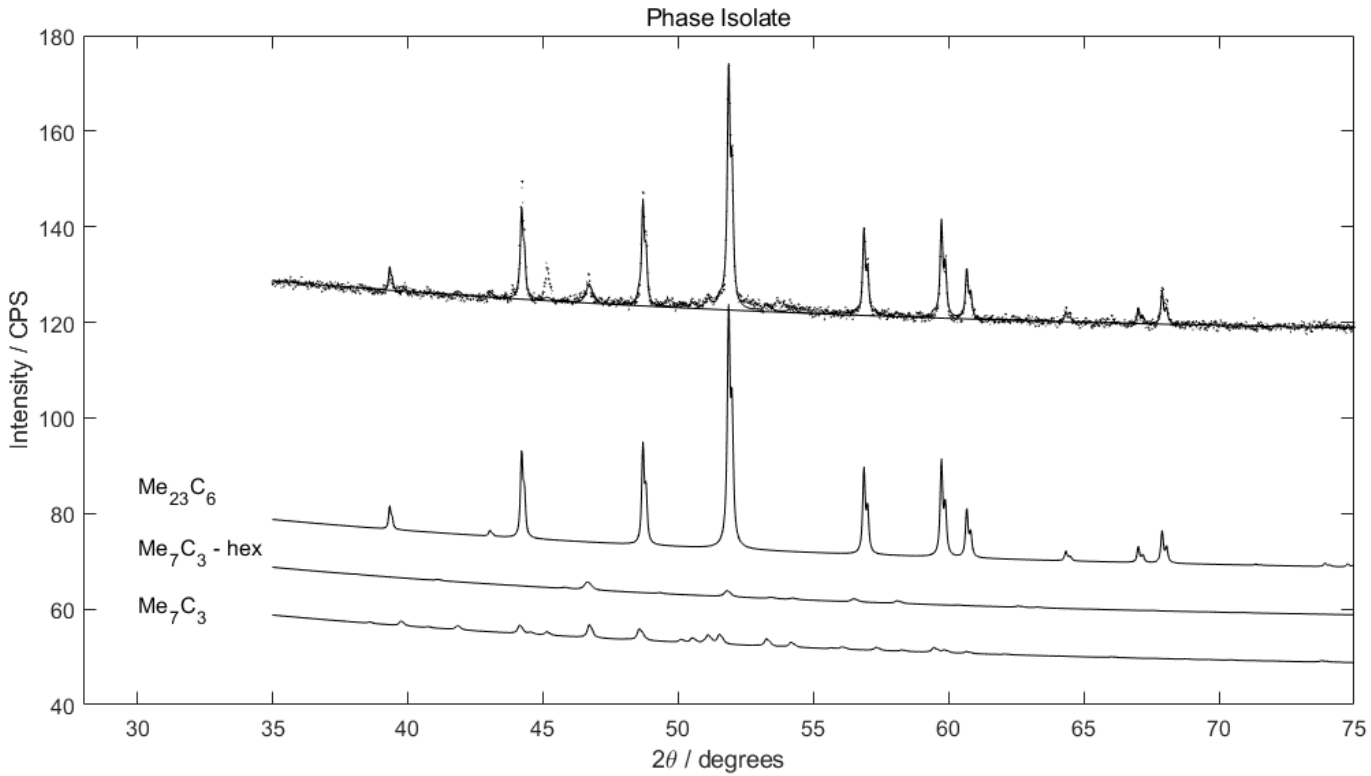


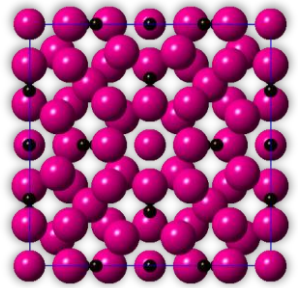
Cr_7C_3 (ortho)

59.6%

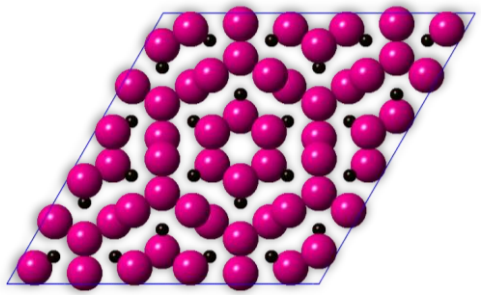
Smeets et al., *Steel Res. Int.* 90 (2019), 1800300

Powder QPA

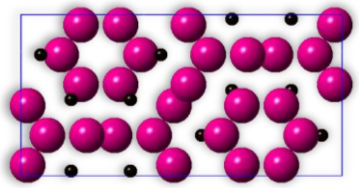




$M_{23}C_6$
XRPD: 84.49 %
SerialED: 33.7 %



M_7C_3 (hex)
XRPD: 3.09 %
SerialED: 6.4 %



M_7C_3 (ortho)
XRPD: 12.42 %
SerialED: 59.6 %

Smeets et al., *Steel Res. Int.* 90 (2019), 1800300

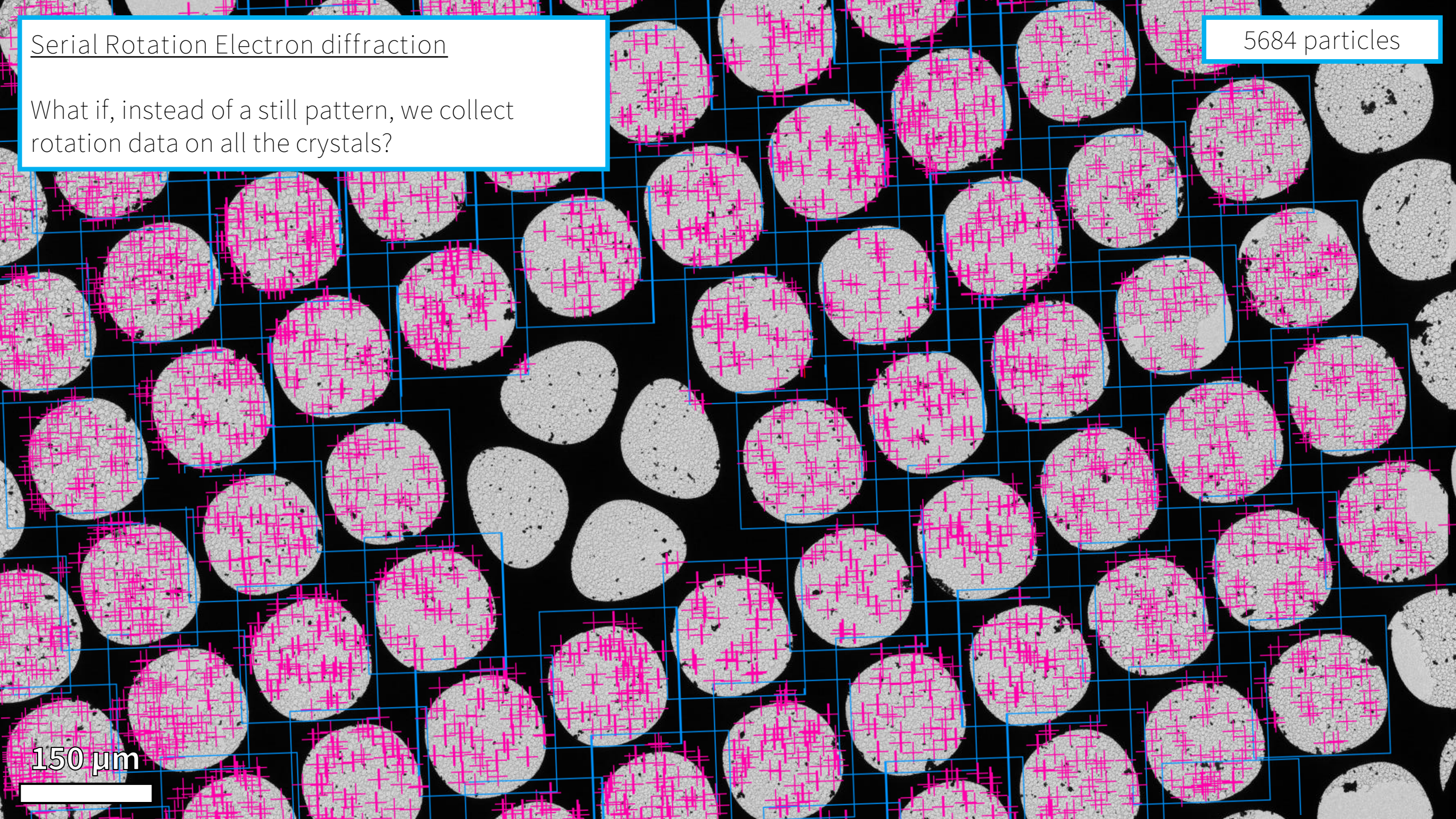
Summary SerialED

- SerialED data: crystal counts
- XPRD data: bulk composition

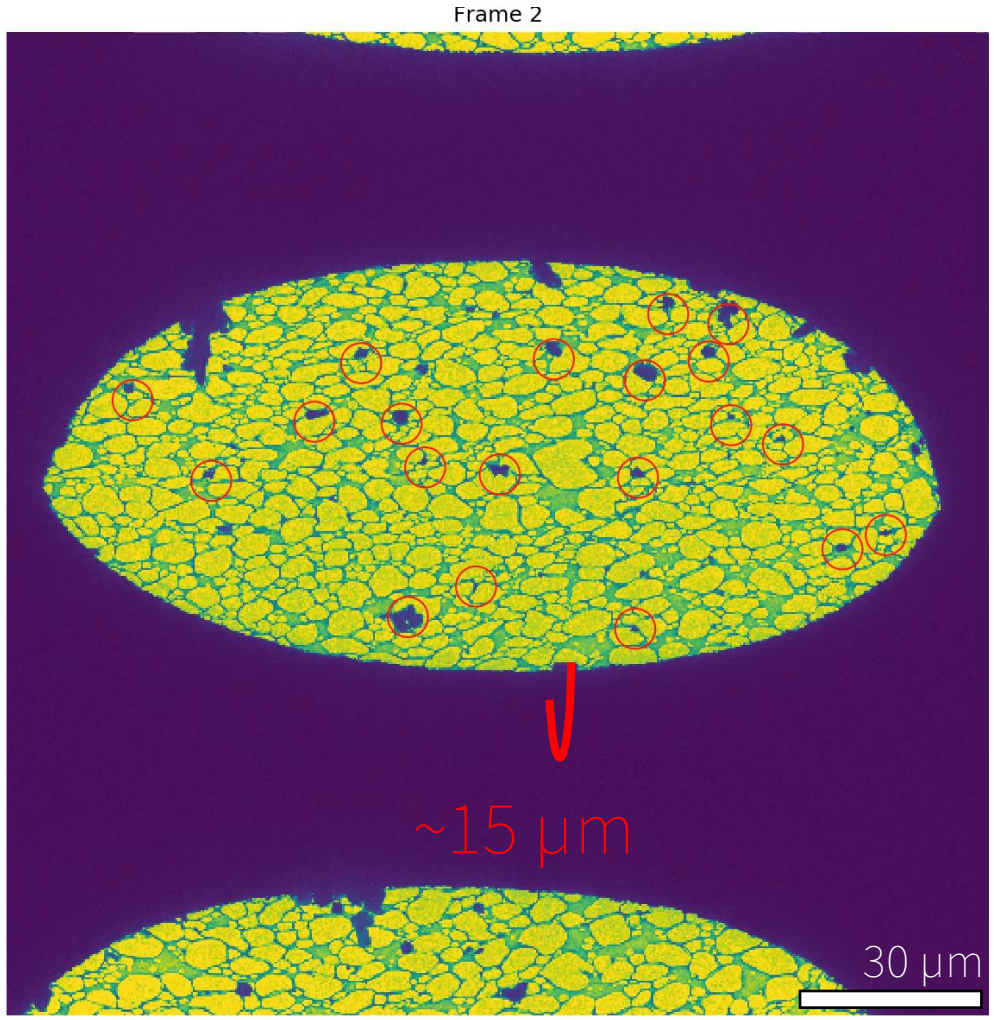
- Indexing still ED frames is an unsolved problem(?)
- Difficult to beat simplicity of XRPD

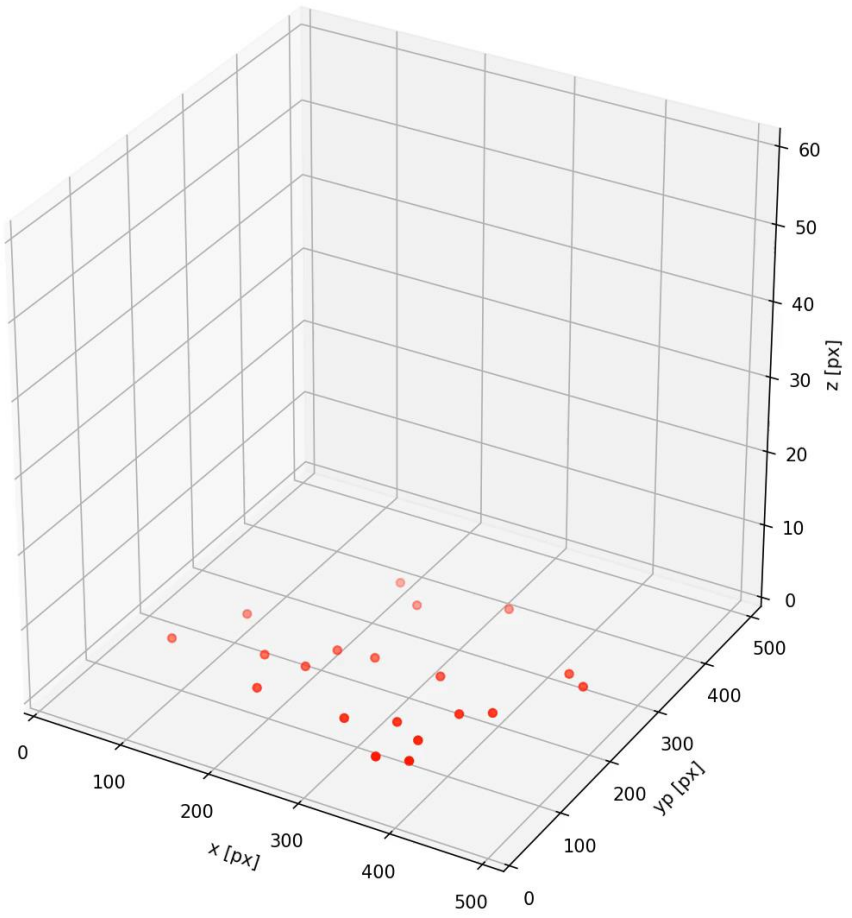
Serial rotation electron diffraction

Can we do phase identification using electron diffraction?


Serial Rotation Electron diffraction
What if, instead of a still pattern, we collect rotation data on all the crystals?
5684 particles
150 µm

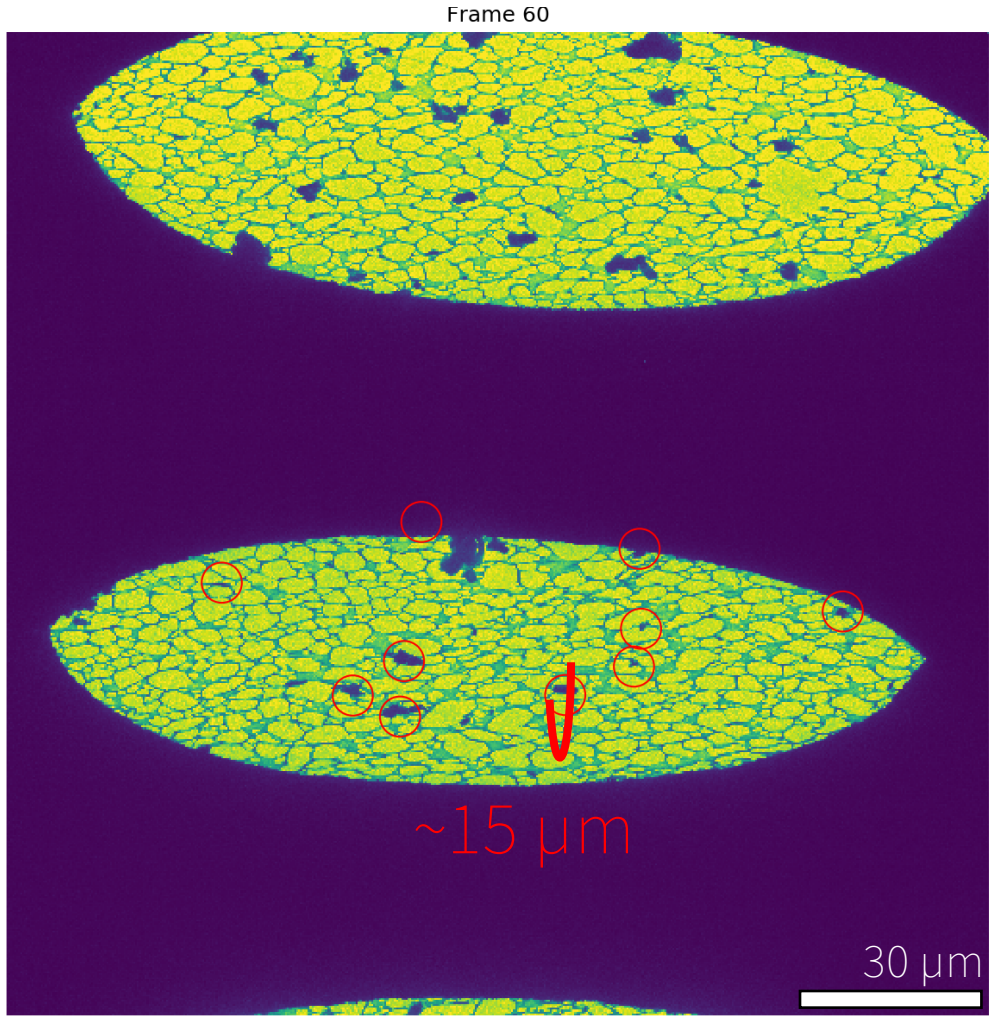
The crystal tracking problem

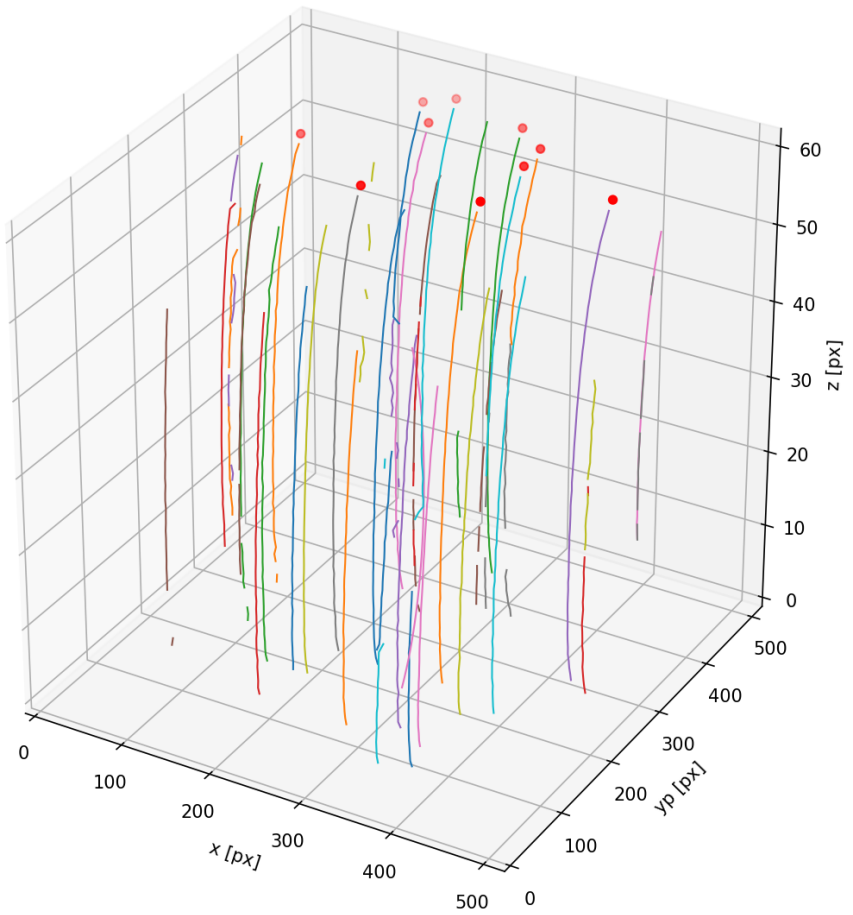




Crystal movement

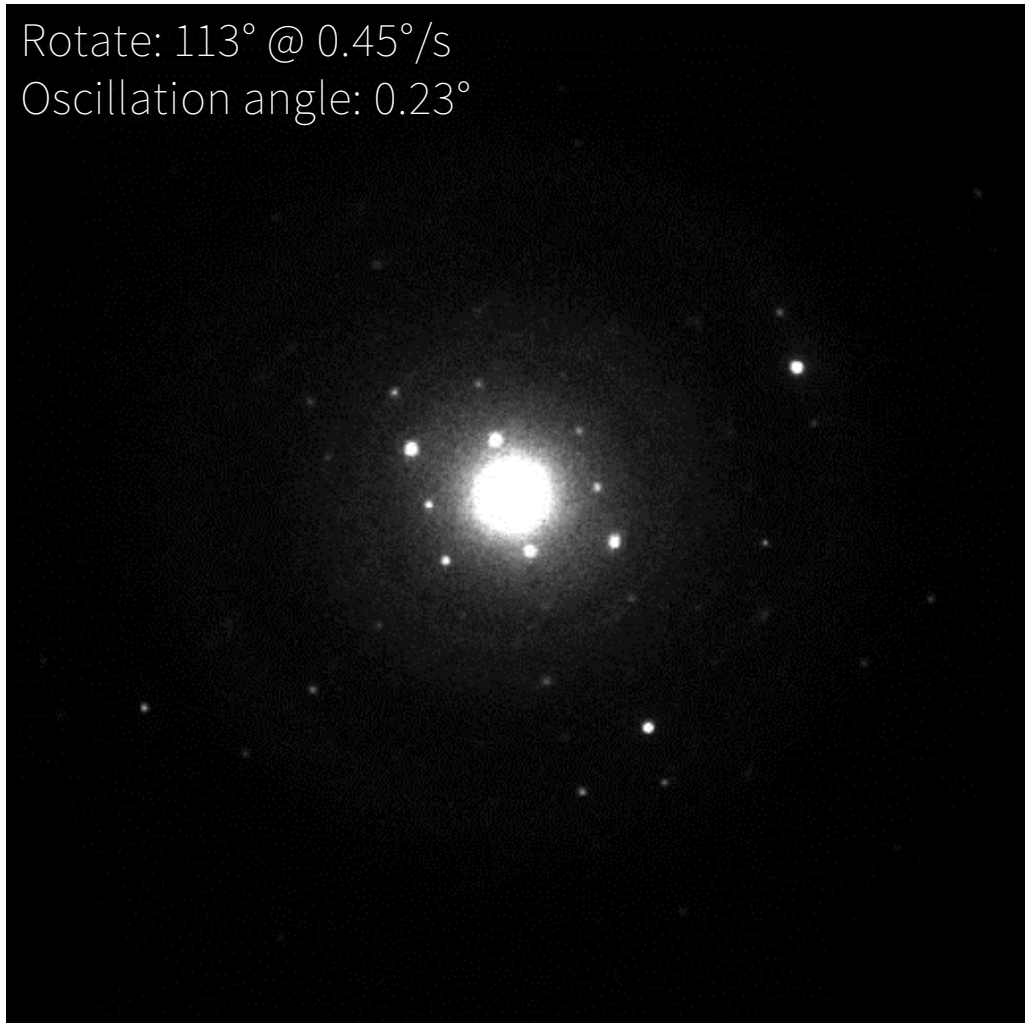
The crystal tracking problem





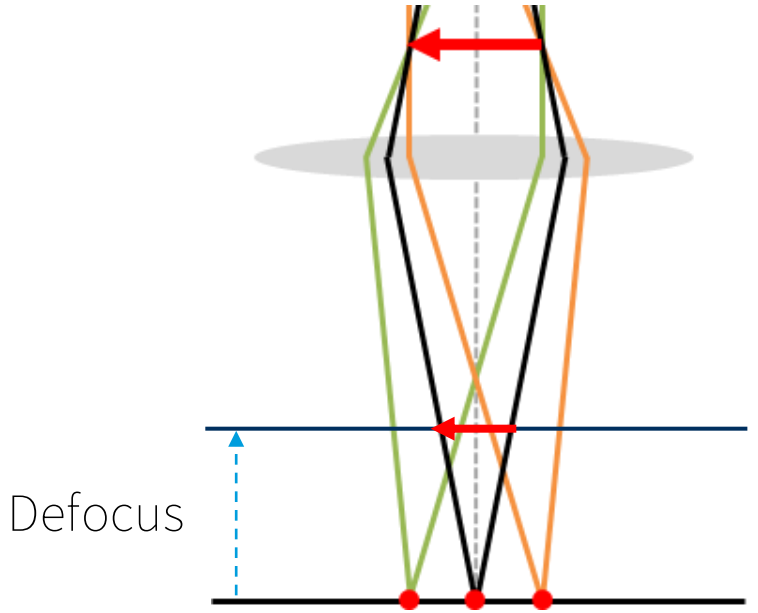
Crystal movement

Using defocus for tracking



Tracking

- Defocus every 10th image (IL1)
- Manually control stage position



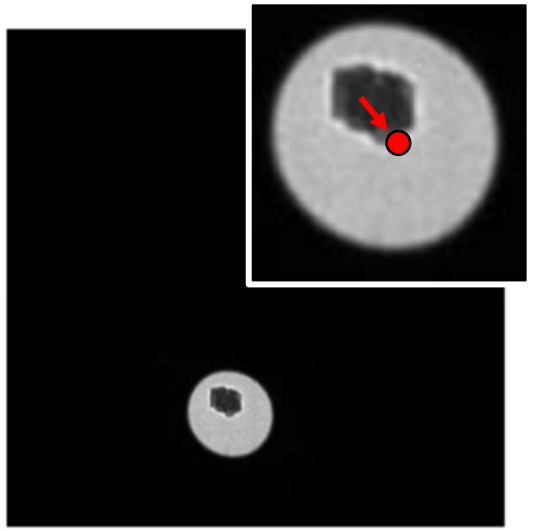
Cichocka *et al.*, *J. Appl. Crystallogr.* 51 (2018): 1652–61

Automated crystal tracking strategy

Frame 1 (500 ms)

Frame 9

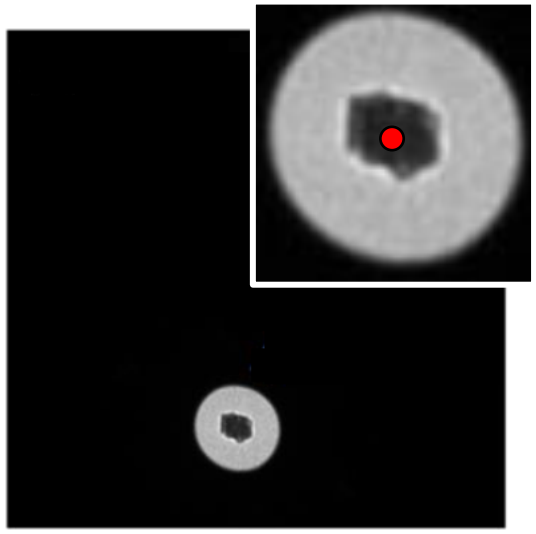
Defocus DP



Frame 10 (20 ms)

Calculate $d(x, y)$ via image analysis

Center crystal via deflectors



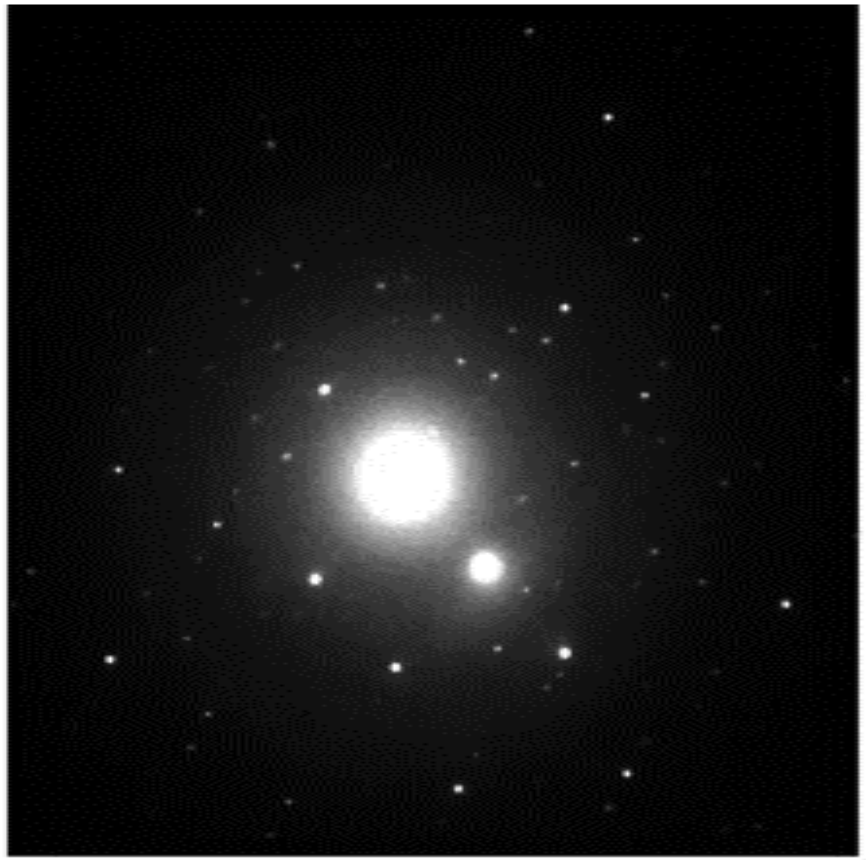
Refocus DP + wait until 500 ms passed

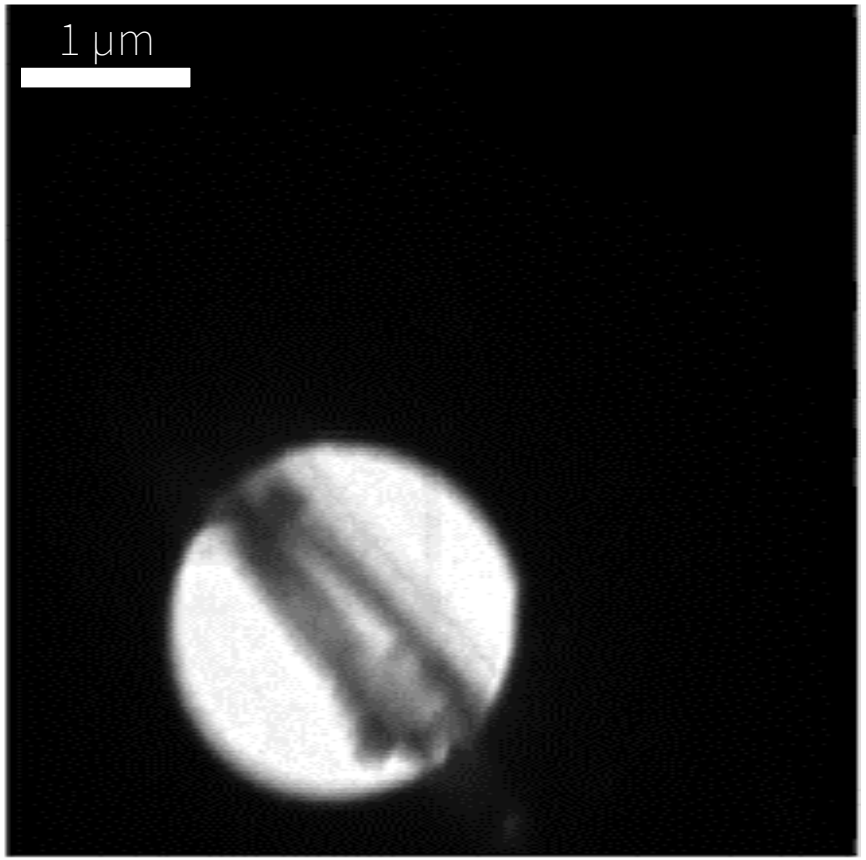
Continue data collection

Frame 11

Wang *et al.*, *IUCrJ* 6 (2019), 854-867

Automated crystal tracking strategy



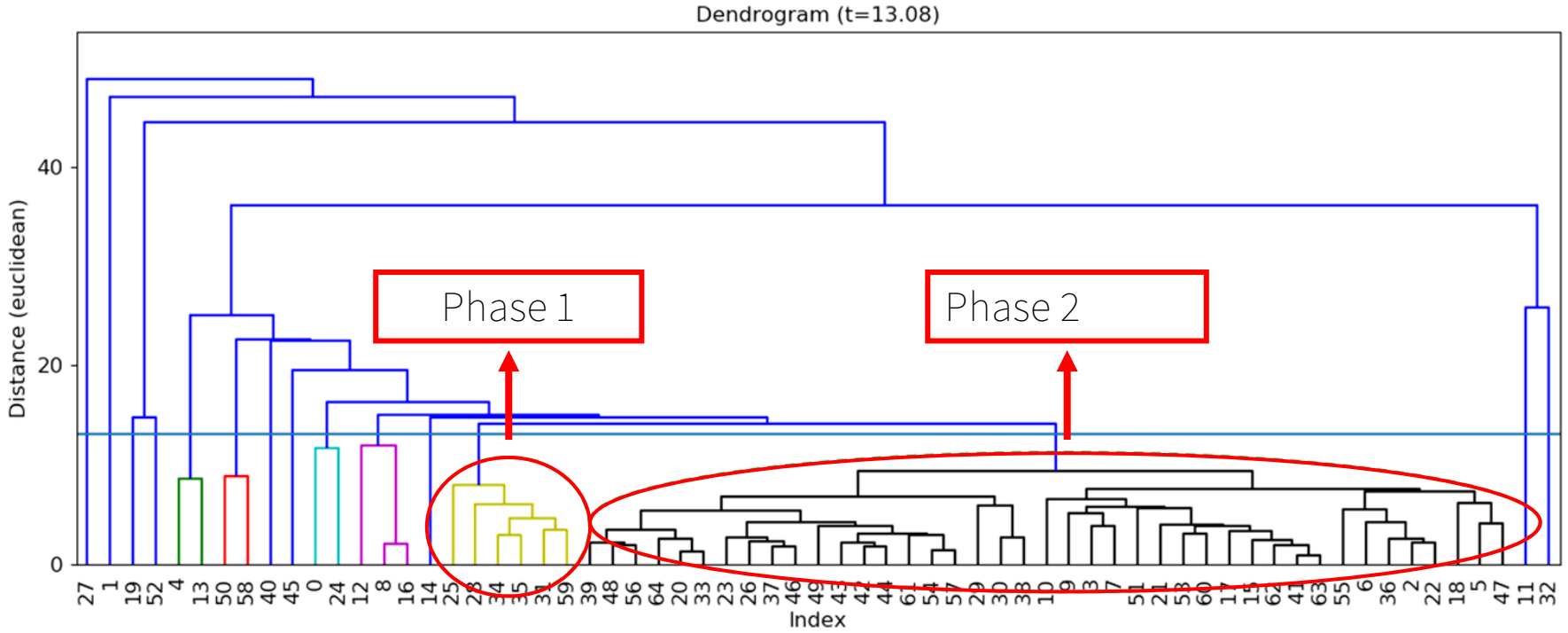


JEOL 2100-LaB_6 @ 200 kV (Timepix)
Rotation: -44.0 to 47.4° @ 0.76°/s (91.4°)
Exposure: 0.5 s, oscillation angle: 0.39°

Wang *et al.*, *IUCrJ* 6 (2019), 854-867

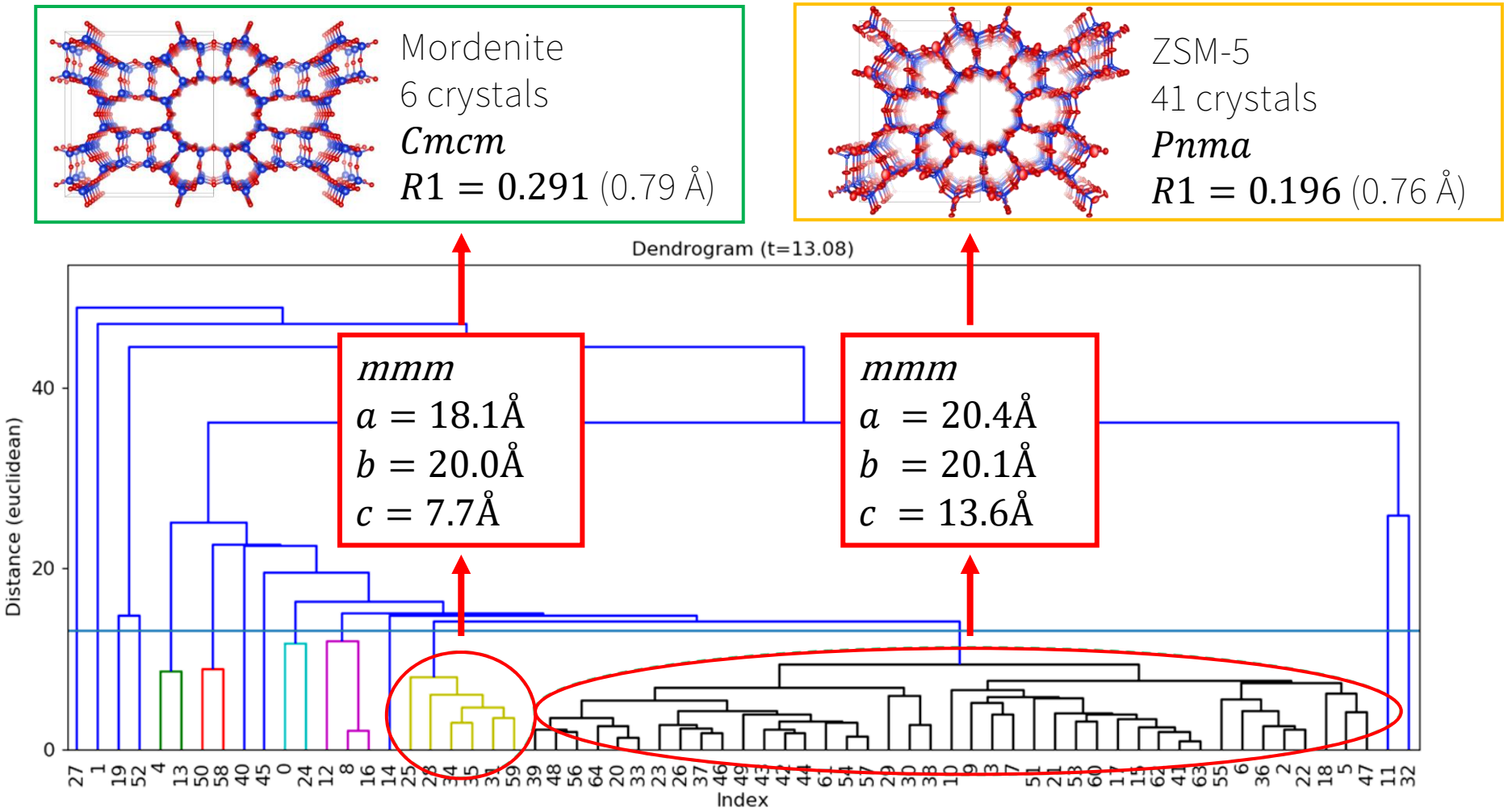
Lattice-based clustering

- Polycrystalline mixture of 2 phases
- SerialRED data from 89 crystals indexed using XDS



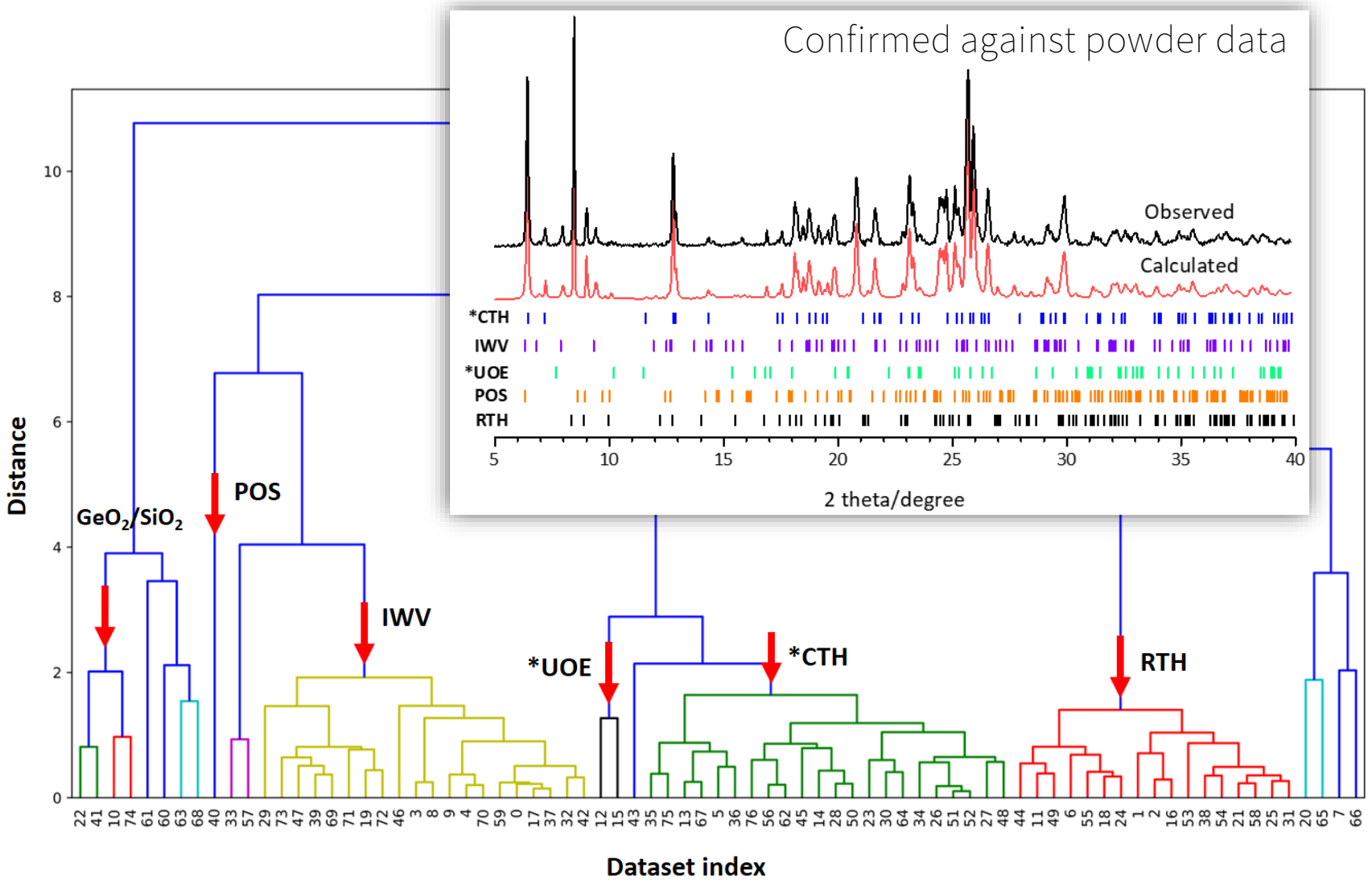
Wang *et al.*, *IUCrJ* 6 (2019), 854-867

Lattice-based clustering



Wang *et al.*, *IUCrJ* 6 (2019), 854-867

Phase identification on a real-world sample



Sample
Single batch
1 organic template

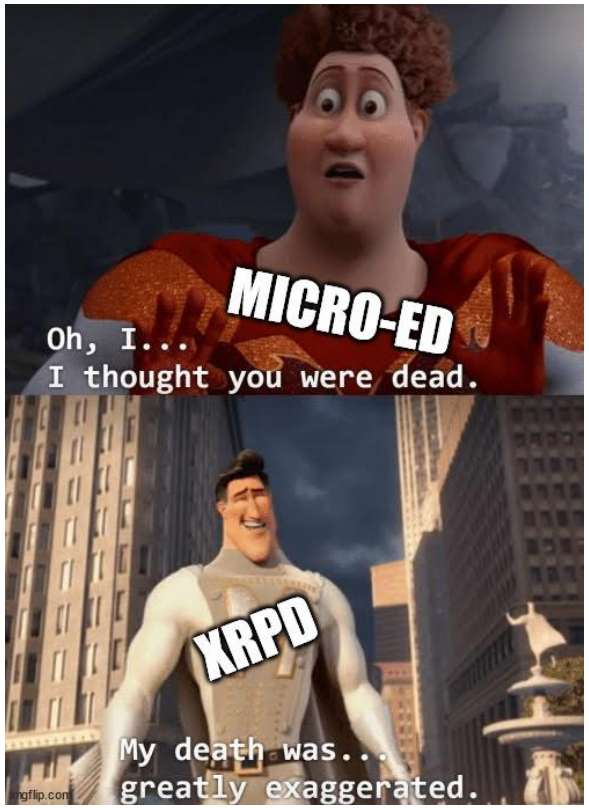
Data collection
JEOL 2100
Timepix camera

7 hours measurement
321 crystals
122 >20° rotation
74 Indexed (DIALS)

Yi Luo (Stockholm University)

In the age of electrons, do we still need powder diffraction?

In the age of electrons, do we still need powder diffraction? – Absolutely!



- The data are mostly complementary
- XRPD methods are well-established for bulk material characterization
- Structure determination from XRPD data only has always been difficult
- ED data are great for single-crystal structure determination
- Potential for applying ED to phase identification problems
- Choice of method depends on the question

netherlands eScience center

Let’s stay in touch

www.eScienceCenter.nl

info@esciencecenter.com

+31 (0)20 460 4770