Serial Crystallography using Electron Diffraction

Stef Smeets

Dept. of Materials and Environmental Chemistry

Stockholm University, Sweden

Stockholm
University

Serial crystallography

- Randomly oriented crystals

- 1 crystal = 1 diffraction pattern

- Collect and combine data on large number of crystals

- Single-crystal-like data set

Why use a TEM for serial crystallography?

- Electron beam is very intense

- Crystals can be located directly

- All images contain information

- There is one in many labs
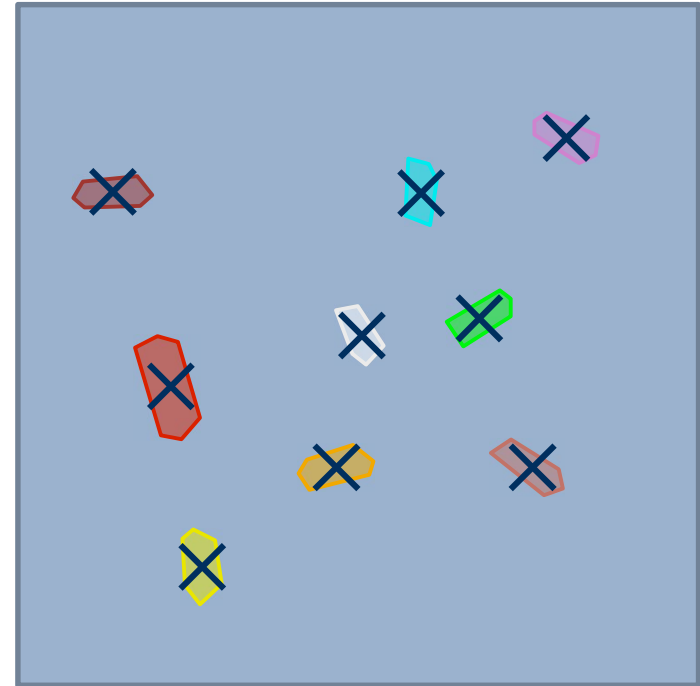
Advantages of serial electron diffraction

- Beam damage is avoided

- No (re)alignment required

- No rotation needed

- Fully automatic data collection

> **Develop serial crystallography using electron diffraction for beam-sensitive materials**

- Organic/inorganic materials, pharmaceuticals
- Small unit cells (<25000Å)

Challenges

- Data collection
  - How to collect ED data on 500-5000 crystals?
  - How to locate and shoot crystals automatically?
- Indexing
  - Can single frames be indexed reliably?
- Data processing
  - How to merge and scale data collected on a large number of crystals?
- Structure solution
  - Are the data good enough for structure determination?
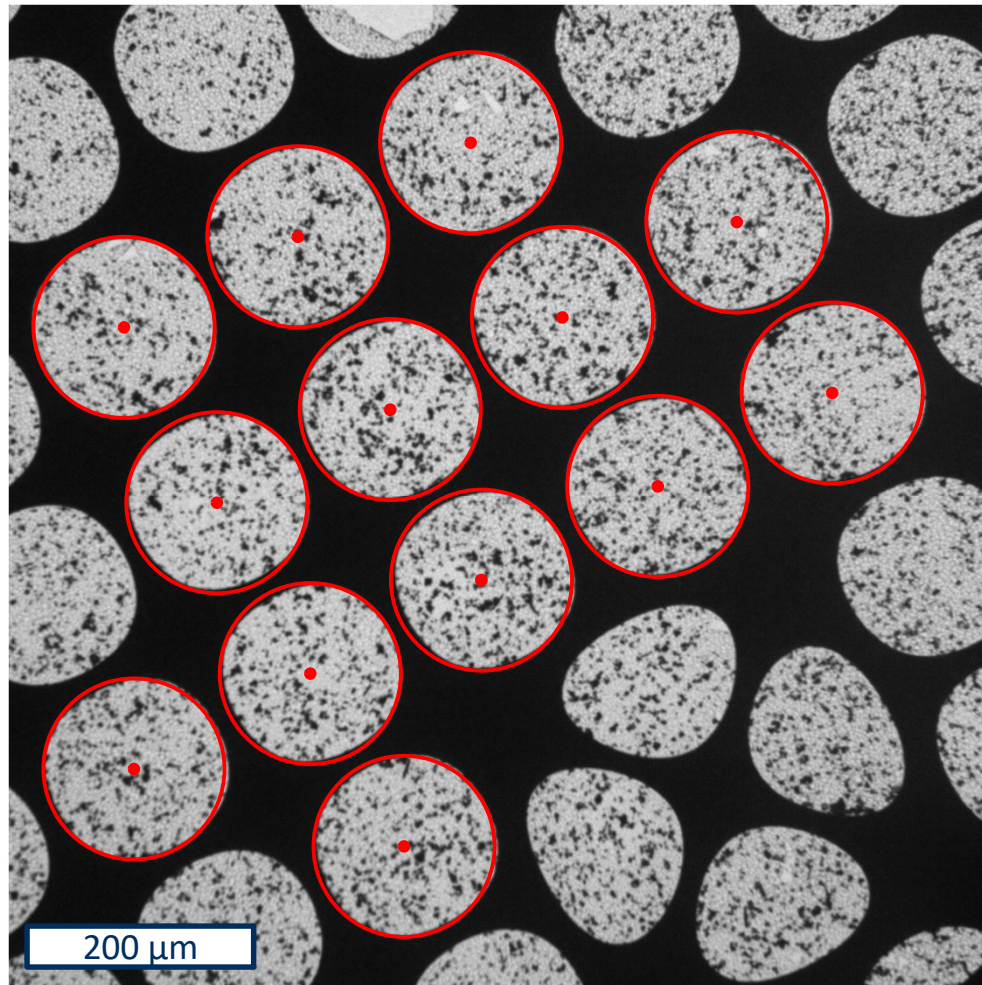
Data collection: mapping the grid
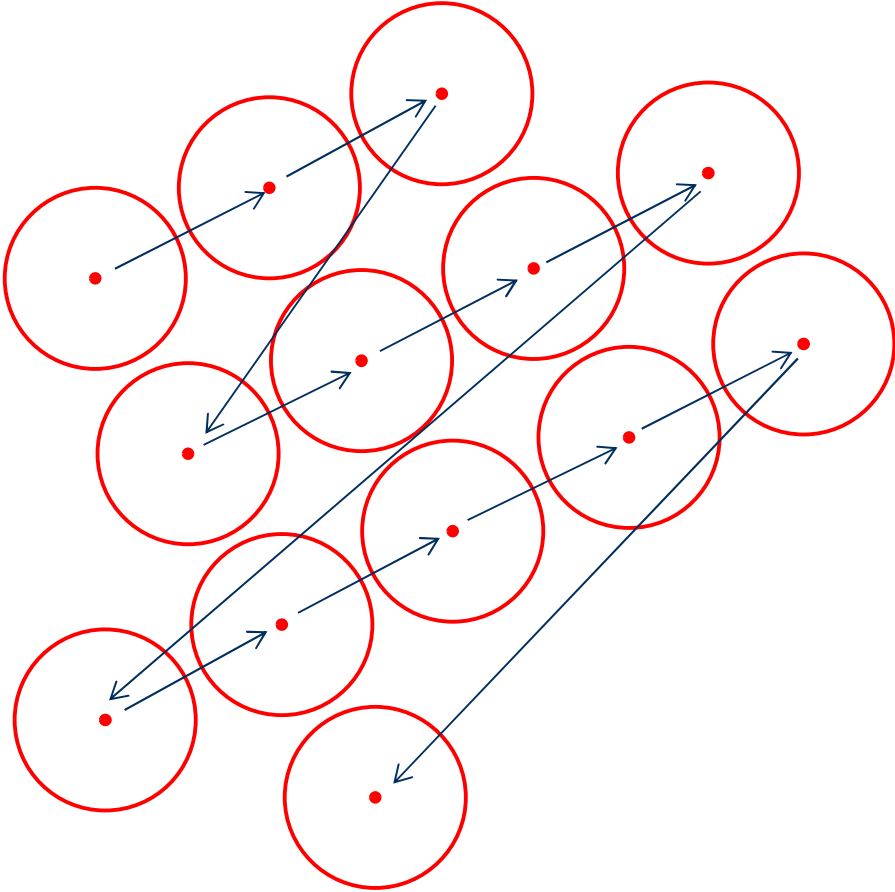

200 µm
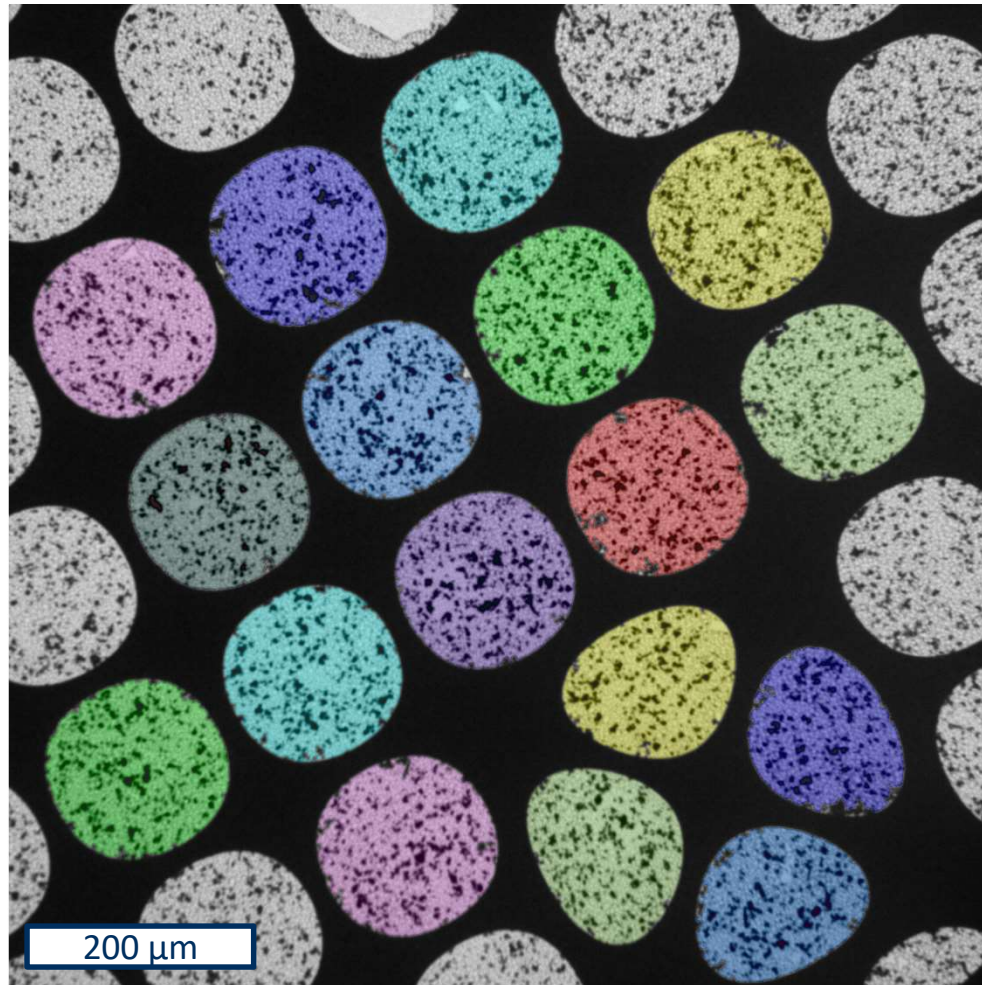
100x magnification
150µm holes

JEOL JEM2100-LaB$_6$
200 kV
Orius CCD

Image processing:
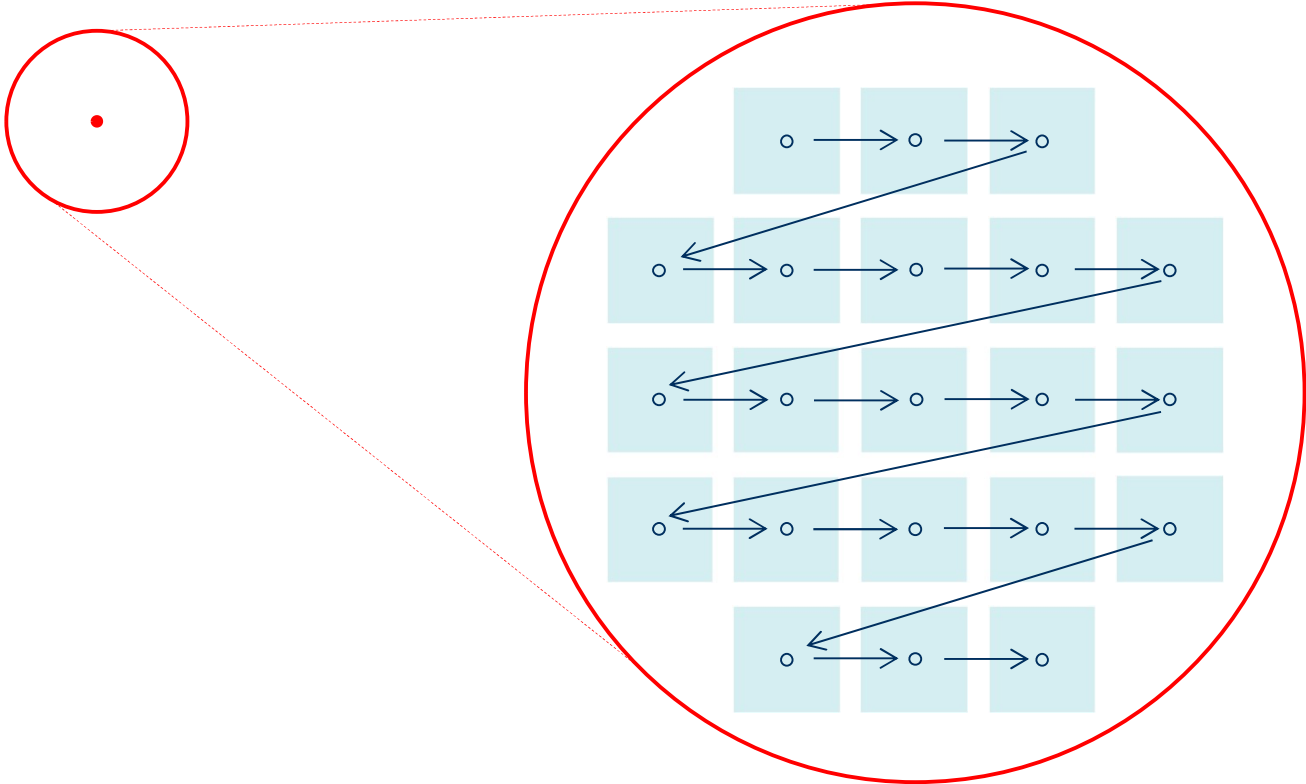scikit-image

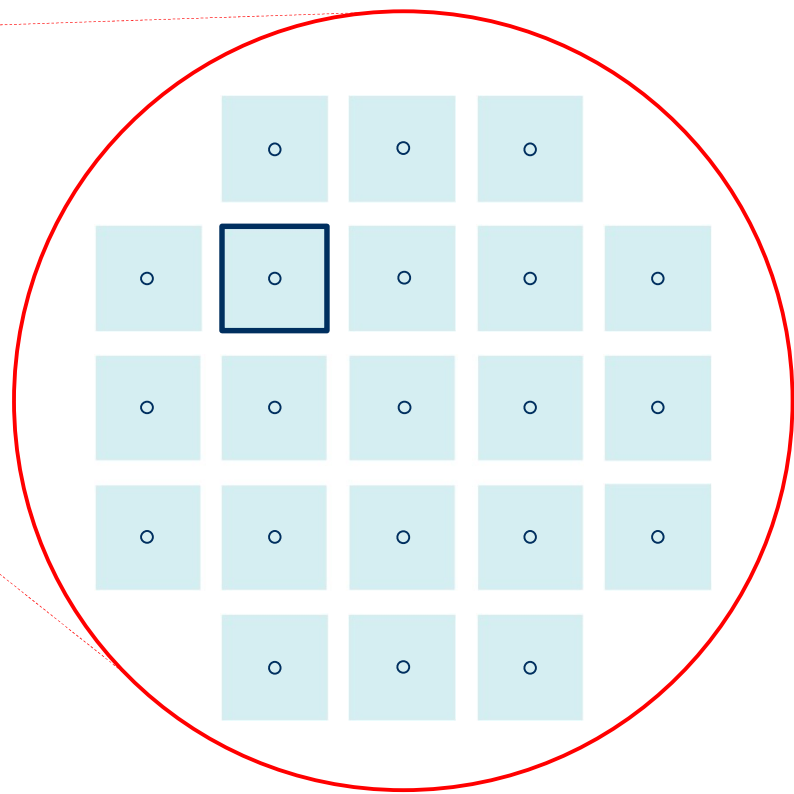# Data collection: map the grid

200 μm

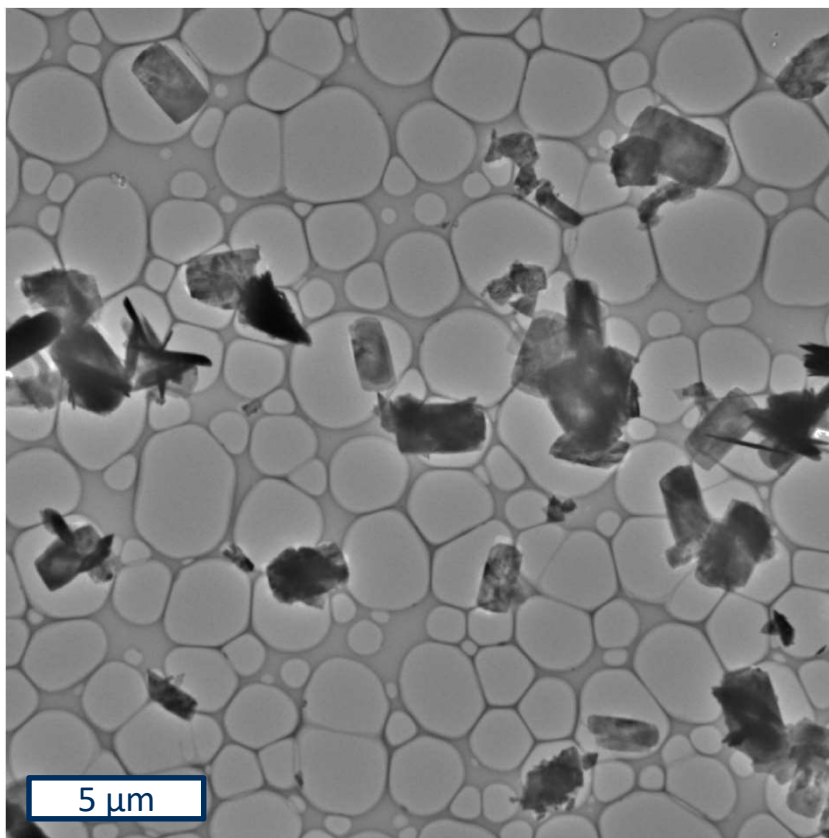# Data collection: map the grid

Data collection: map hole

Data collection: find crystals

2500x magnification

5 μm

Data collection: diffraction

- Beamshift -> Focused nanobeam to collect ED data

- Potentially: 13 holes x 21 positions x 20 crystals = 5500 data sets
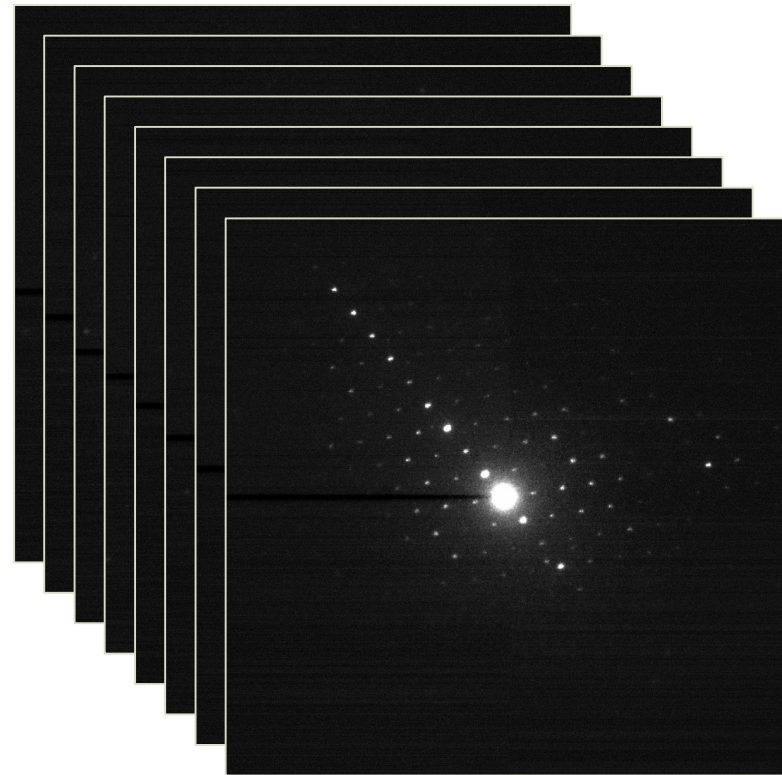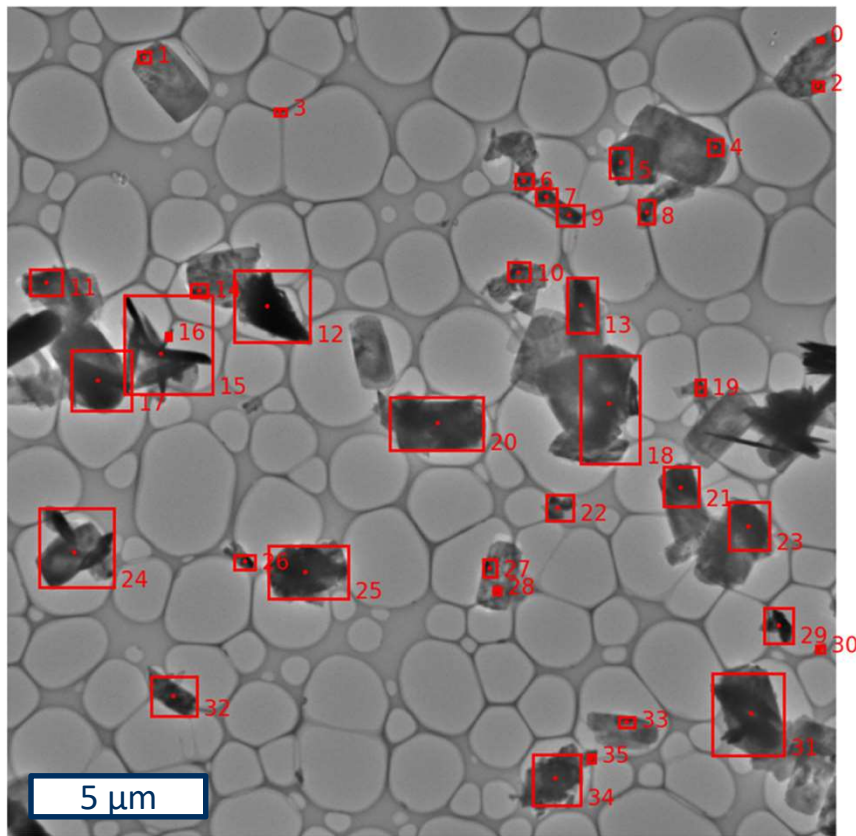
Indexing

Challenges

- Get accurate crystal orientations from a single frame
- Small unit cells (limited number of reflections)
- Crystals can overlap
- Find criteria to accept/reject orientations

- Assume unit cell is known

Indexing

zoom 1

Min 94 Max 485684 Mean 211.863   52 %   1419, 769   206

100 µm
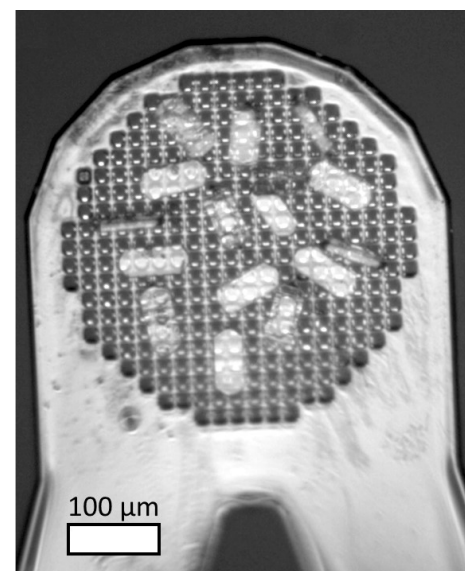
15 crystals of ZSM-5

SNBL (ESRF), φ-scan, 1° / step
4.6% bandwidth

C. Dejoie, S. Smeets *et al.* (2015) *IUCrJ* **2**, 361

Indexing: peak finding

zoom 1

Min 94 Max 485684 Mean 211.863   52 % 1377, 1661   194.5

15 crystals of ZSM-5

100 μm

548 reflections

Indexing: brute force algorithm
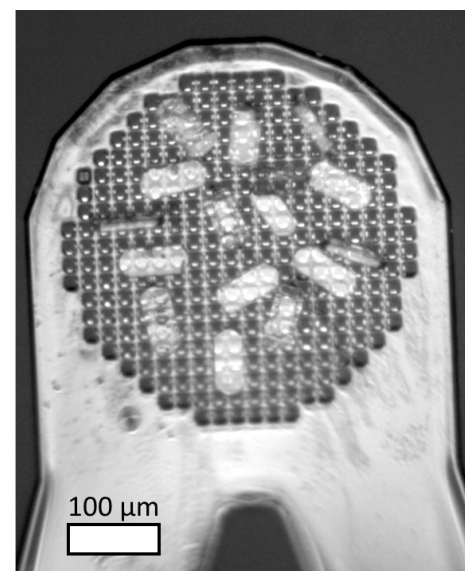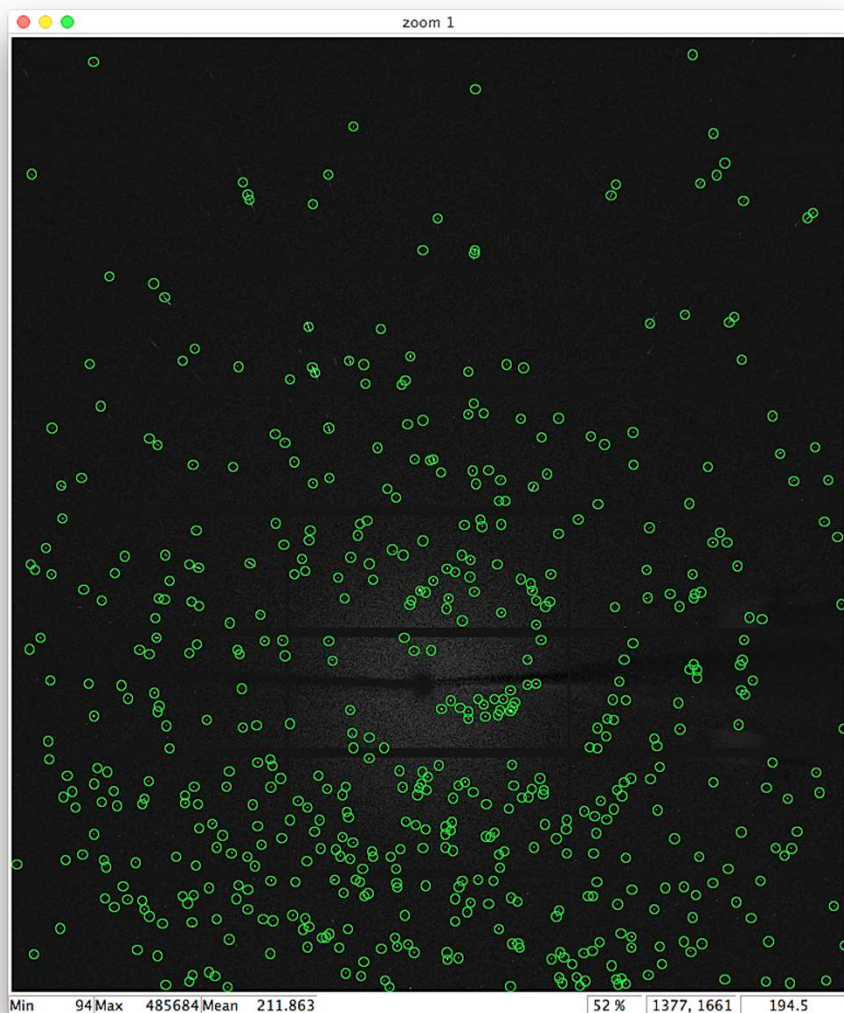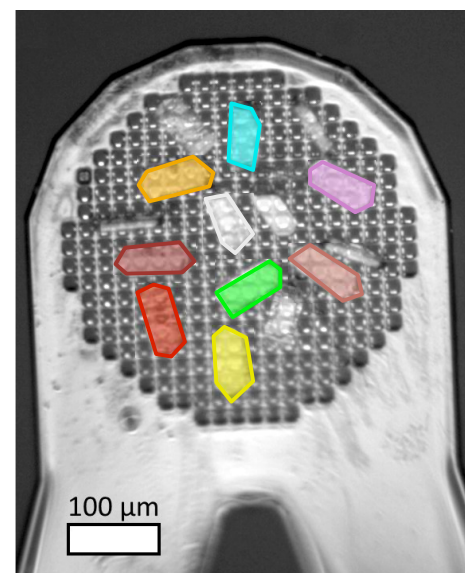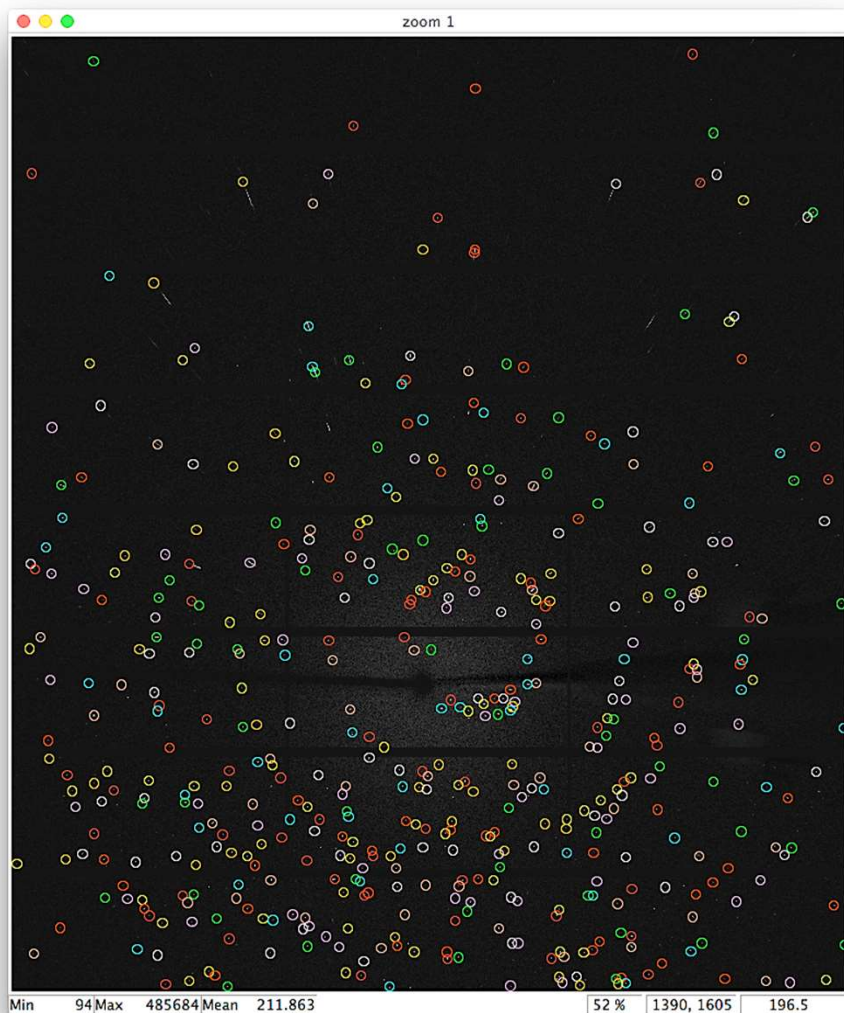
15 crystals of ZSM-5

548 reflections (9 crystals)

C. Dejoie, S. Smeets *et al.* (2015) *IUCrJ* **2**, 361

Indexing: single frames

Tests using single-crystal rotation electron diffraction (RED) data
Tilt range: ~120°

sample	space group	volume (Å³)	# frames	indexed
Garnet	*Ia*-3*d*	1737	1204	96%
ZSM-5	*Pnma*	5327	1471	90%
Ni-Se-O-Cl system[1]				

[1]Y. Yun *et al.* (2014) *J. Appl. Cryst.* **47**, 2048

Indexing: phase matching

Tests using RED data on multiphase Ni-Se-O-Cl system
Tilt range: ±15° (300 frames)
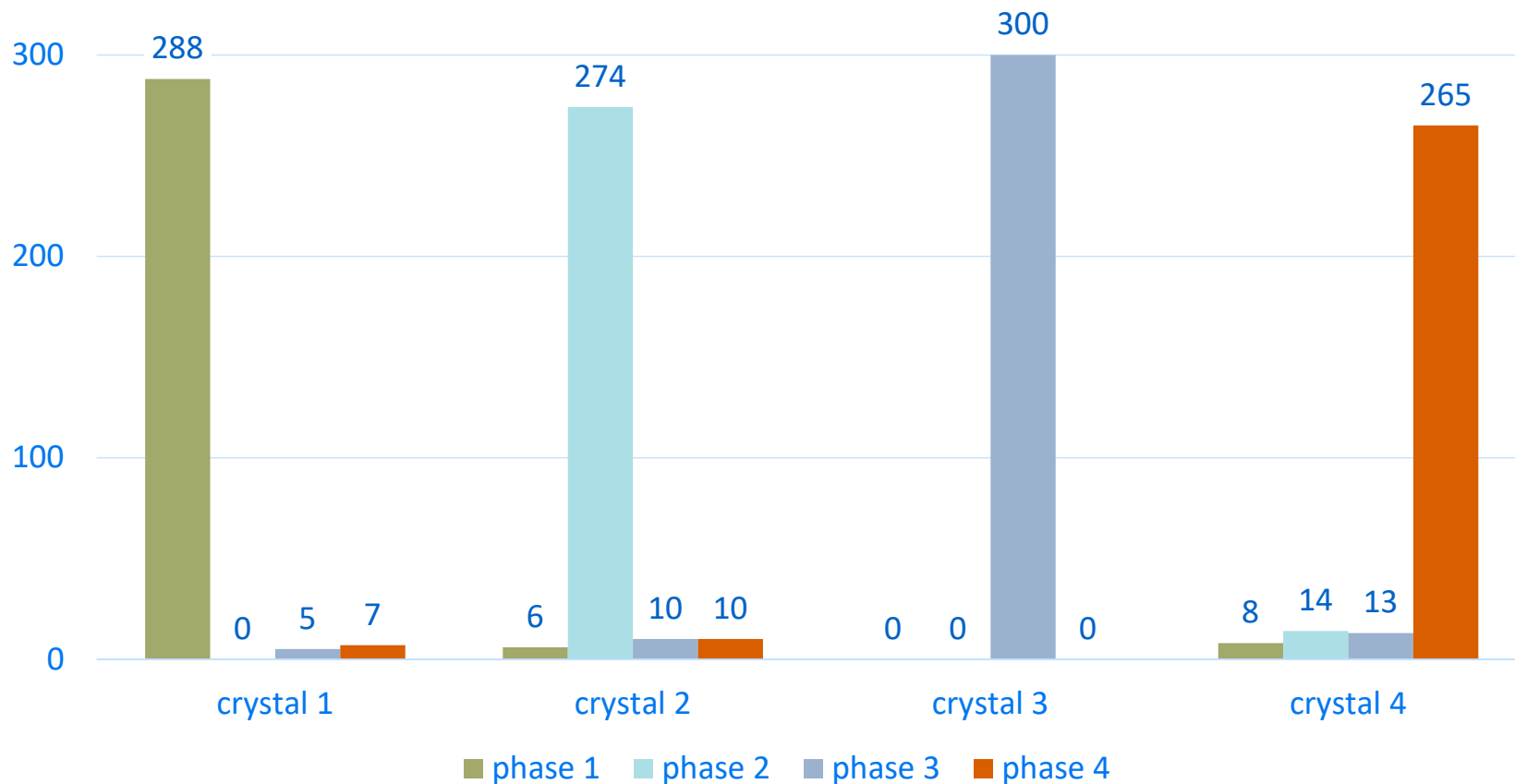
Data processing: merging & scaling

How to merge *hkl* listings of 500+ data frames?

Challenges

- Variations in diffracting volume (scaling)

- Dynamical scattering

- Missassignment of reflection indices

- Partial intensities

- *Structure solution of oxides from zone axes precession diffraction data* (Klein, Z. Kristallogr., 2012)

- *Refining structures against reflection rank: an alternative metric for electron crystallography* (Eggeman & Midgley, Acta Cryst. A, 2012)

Data processing: ranking

- *SerialRank: Spectral Ranking using Seriation* (Fogel *et al.*, ArXiV, 2014)

Data processing: ranking

- *SerialRank: Spectral Ranking using Seriation* (Fogel *et al.*, ArXiV, 2014)

h k l	Frame 1 Rank	Frame 2 Rank	Frame 3 Rank	Frame 4 Rank	Frame 5 Rank	Combined Rank
3 1 1	1	4	1	4	1	2
3 1 3	3	7	3	1	3	3
0 0 2	2	1	2	3	2	1
1 1 7	4	2	4	2	5	4
1 3 1	5	6	9	10	4	6
2 2 2	6	3	5	9	6	5
1 1 3	9	10	6	7	8	8
1 1 1	7	5	10	5	7	7
1 1 5	10	8	7	6	10	9
2 0 2	8	9	8	8	9	10

Strong ↓ weak

- Find rank -> Assign intensities based on reflection rank

Data processing: conventional merge

- 500 simulated frames on zeolite SSZ-58

- Partial intensities, $d_{min}=1$Å, 2250 uniq. refs.

- Random scale

SSZ-58: n=500, r=0.0, c=0.988

SSZ-58: n=500, r=0.0, c=0.989
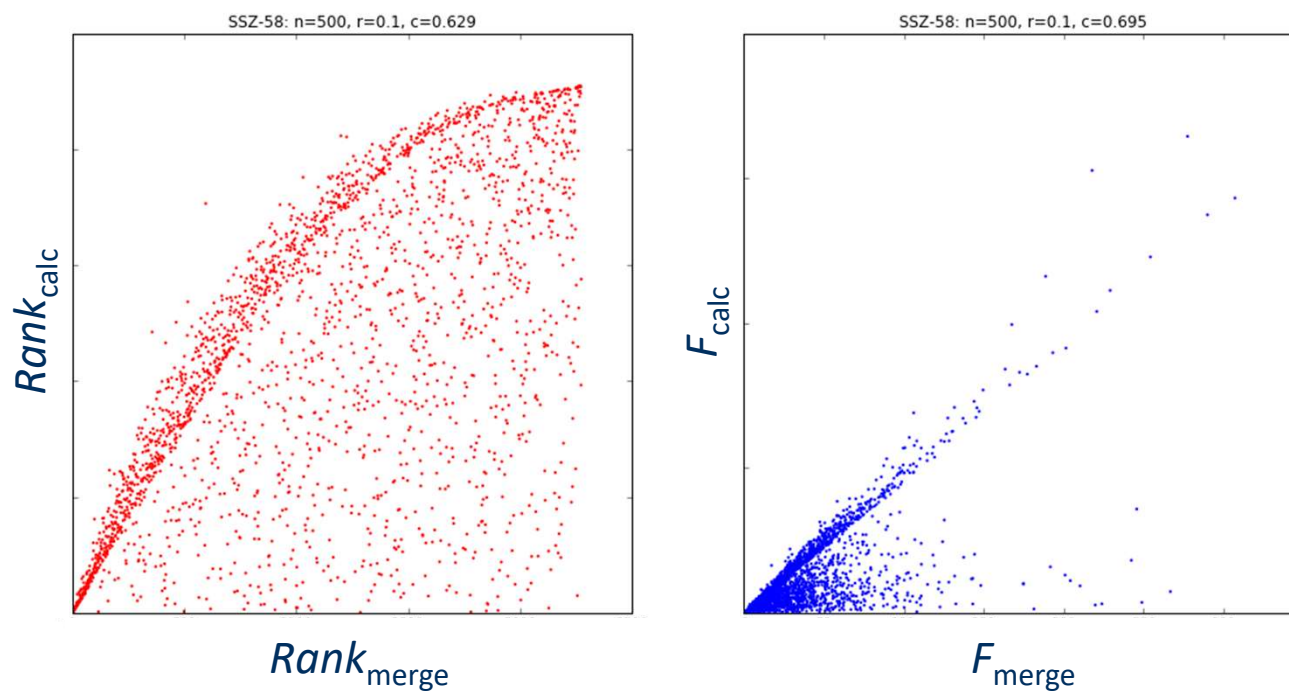
$Rank_{calc}$

$Rank_{merge}$

F_{calc}

F_{merge}

Data processing: conventional merge

- 500 simulated frames on zeolite SSZ-58

- Partial intensities, $d_{min}=1\text{Å}$, 2250 uniq. refs.

- Random scale, shuffle 10% of indices

SSZ-58: n=500, r=0.1, c=0.629

$Rank_{calc}$ vs $Rank_{merge}$

SSZ-58: n=500, r=0.1, c=0.695

F_{calc} vs F_{merge}

Data processing: SerialMerge

- 500 simulated frames on zeolite SSZ-58

- Partial intensities, $d_{min}=1$Å, 2250 uniq. refs.

- Random scale

SSZ-58: n=500, r=0.0, c=0.975

SSZ-58: n=500, r=0.0, c=0.913
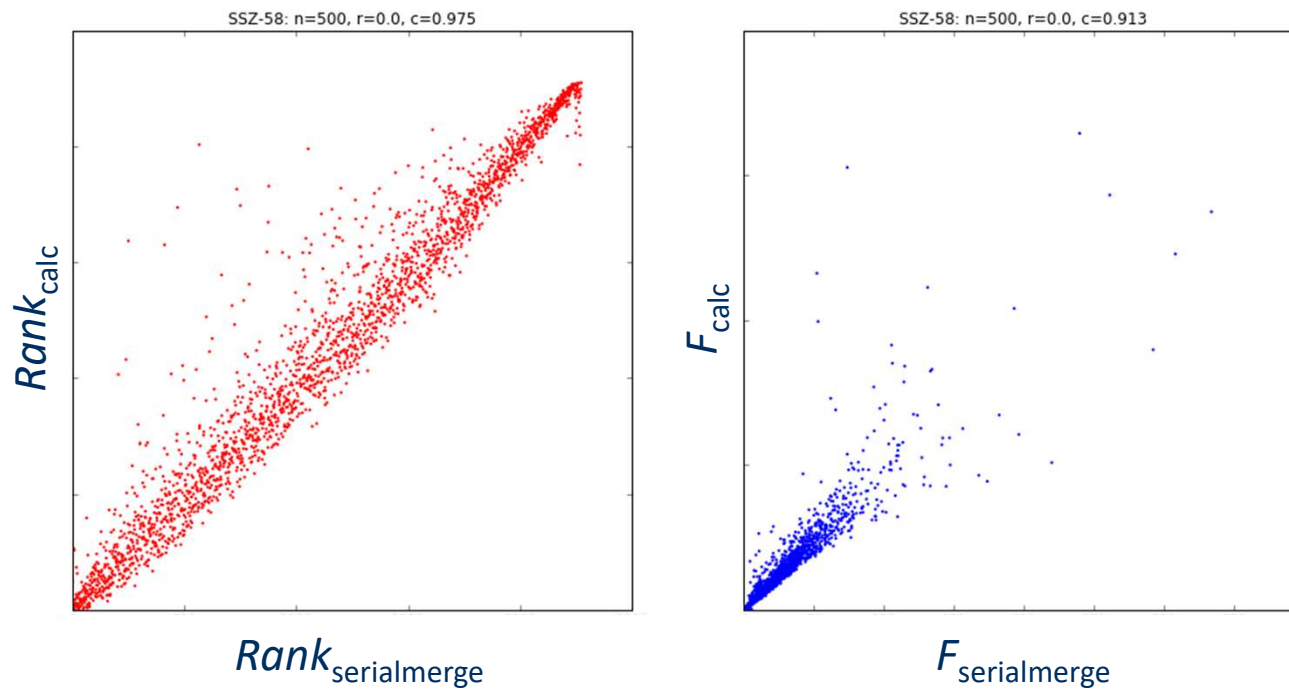
$Rank_{calc}$

$Rank_{serialmerge}$

F_{calc}

$F_{serialmerge}$

Data processing: SerialMerge

- 500 simulated frames on zeolite SSZ-58

- Partial intensities, $d_{min}=1\text{Å}$, 2250 uniq. refs.

- Random scale, shuffle 10% of indices

SSZ-58: n=500, r=0.1, c=0.972

SSZ-58: n=500, r=0.1, c=0.911

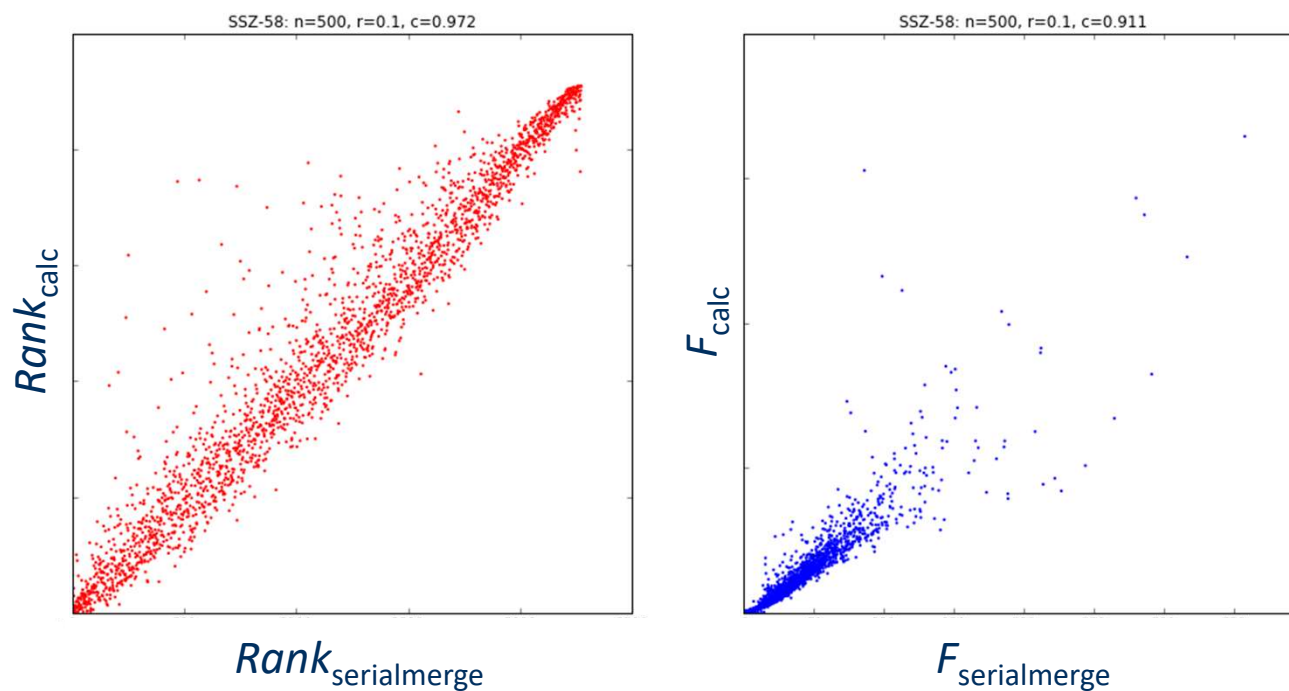$Rank_{calc}$

$Rank_{serialmerge}$
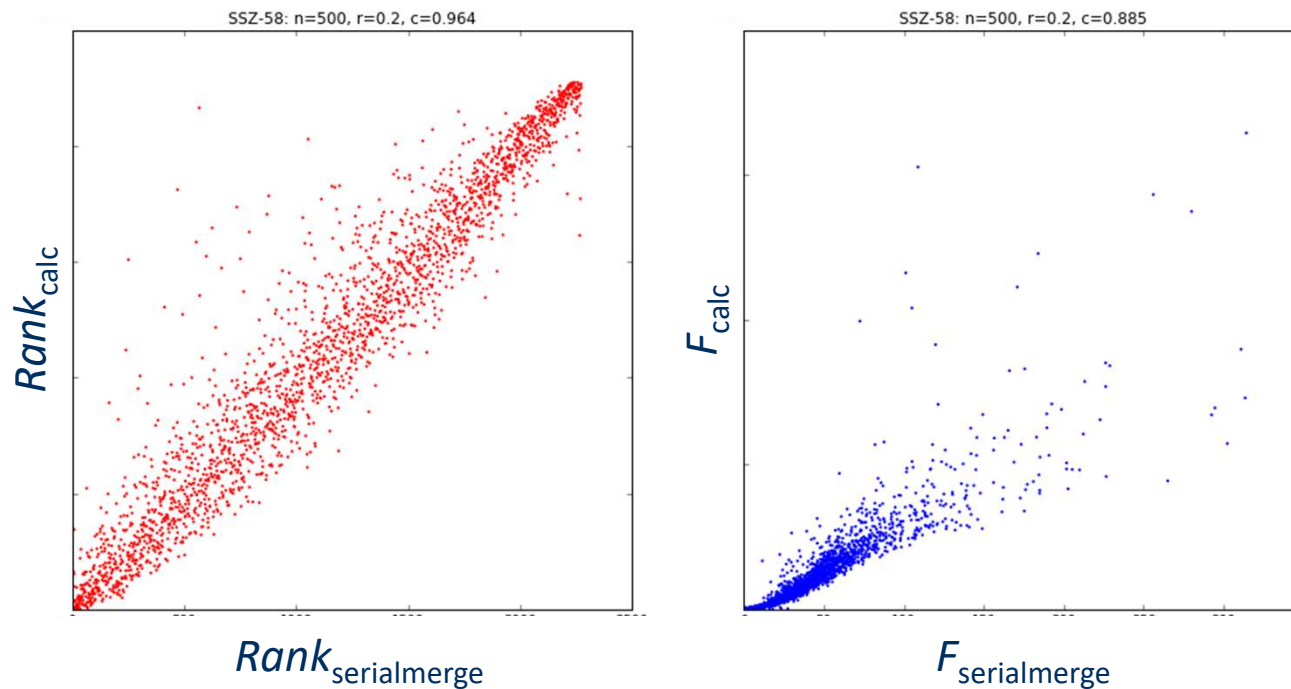
F_{calc}

$F_{serialmerge}$

Data processing: SerialMerge

- 500 simulated frames on zeolite SSZ-58
- Partial intensities, $d_{min}=1\text{Å}$, 2250 uniq. refs.
- Random scale, shuffle 20% of indices

SSZ-58: n=500, r=0.2, c=0.964

$Rank_{calc}$

$Rank_{serialmerge}$

SSZ-58: n=500, r=0.2, c=0.885

F_{calc}

$F_{serialmerge}$

Data processing: SerialMerge

- 500 simulated frames on zeolite SSZ-58

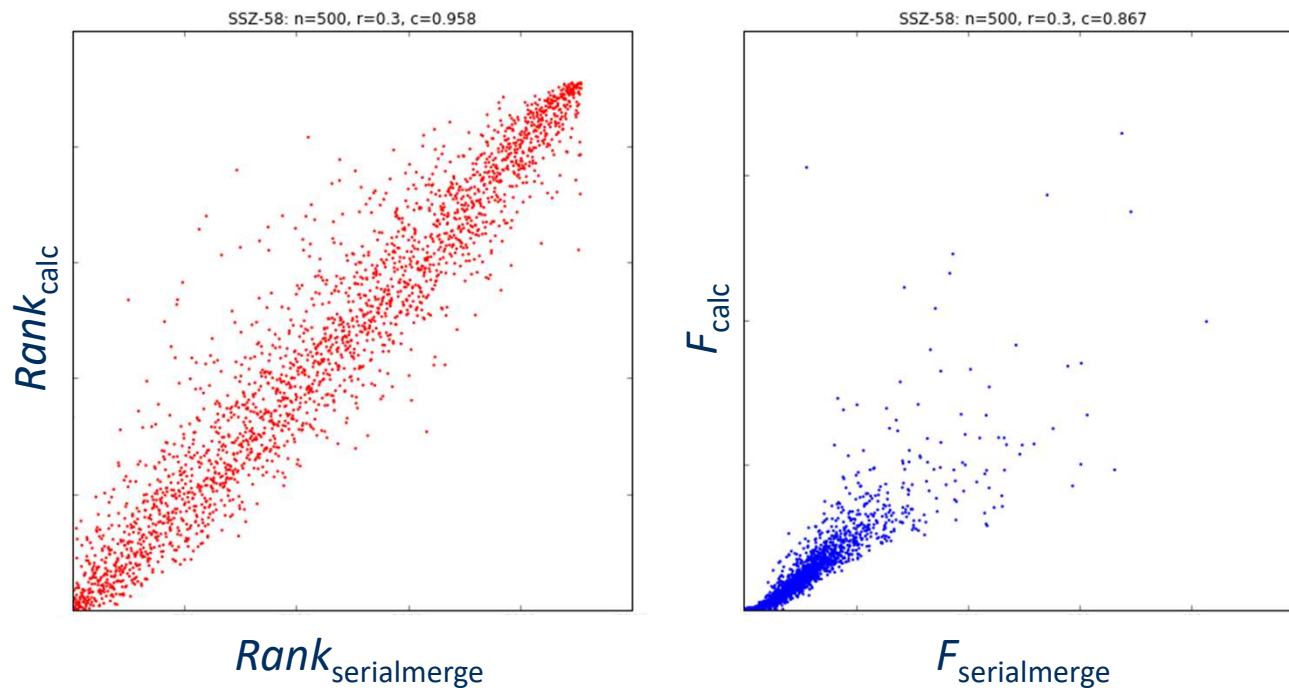- Partial intensities, d_{min}=1Å, 2250 uniq. refs.

- Random scale, shuffle 30% of indices

Data processing: SerialMerge

- 500 simulated frames on zeolite SSZ-58

- Partial intensities, $d_{min}=1Å$, 2250 uniq. refs.

- Random scale, shuffle 40% of indices

SSZ-58: n=500, r=0.4, c=0.946

$Rank_{calc}$ vs $Rank_{serialmerge}$

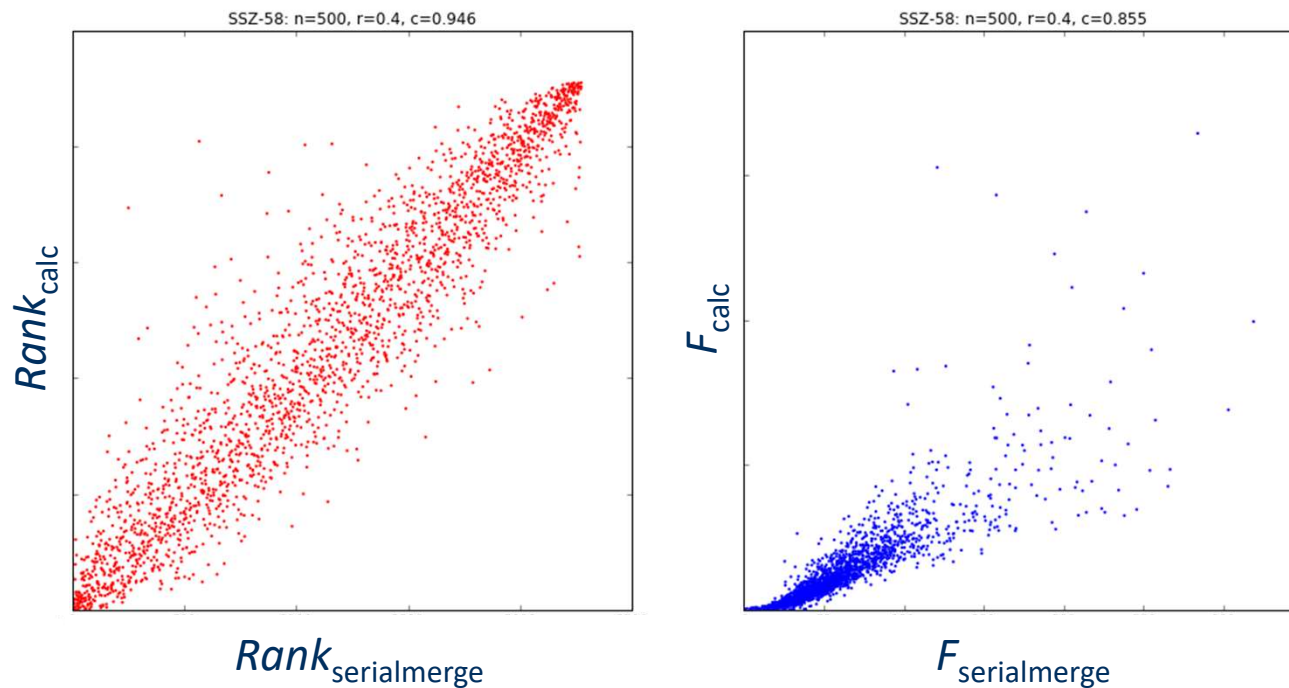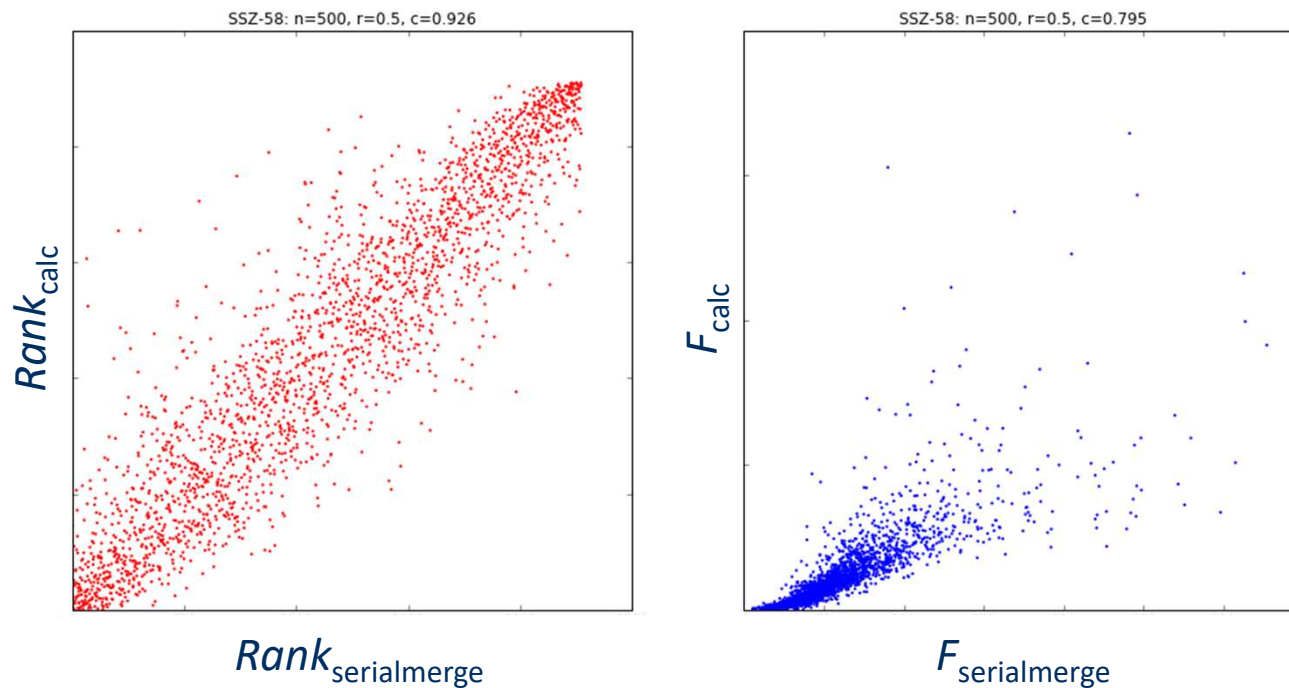SSZ-58: n=500, r=0.4, c=0.855

F_{calc} vs $F_{serialmerge}$

Data processing: SerialMerge

- 500 simulated frames on zeolite SSZ-58

- Partial intensities, $d_{min}=1\text{Å}$, 2250 uniq. refs.

- Random scale, shuffle 50% of indices

SSZ-58: n=500, r=0.5, c=0.926

SSZ-58: n=500, r=0.5, c=0.795

Structure solution: simulated data

- Simulate 500 frames of 6 zeolites

- Random scale, shuffle up to 80% of indices

- Program FOCUS

	# atoms	Spgr	Vol. (Å³)	10%	20%	30%	40%	50%	60%	80%
SSZ-55	11	*C*2221	1396	yes	yes	yes	yes	yes	yes	yes
SSZ-59	24	*P*21*nm*	891	yes	yes	yes	yes	yes	no	no
SSZ-53	25	*C*2/*c*	3562	yes	yes	yes	yes	yes	no	no
SSZ-45	29	*Fmmm*	10697	yes	yes	yes	no	no	no	no
SSZ-58	38	*Pmma*	4051	yes	yes	yes	no	no	no	no
SSZ-56	45	*P*2$_1$/*m*	3277	yes	yes	yes	no	no	no	no

Summary & Conclusions

- Data collection
  - Work in progress

- Indexing
  - Single frames can be indexed reliably

- Data processing
  - SerialMerge algorithm avoids scaling and is insensitive to intensity inaccuracies

- Structure solution
  - Merged data quality good enough for structure determination

- Software
  - Automated data collection: *Instamatic*
  - Data processing/indexing: *SnapKit*

- Applications
  - Structure determination of beam sensitive materials
  - Phase analysis and identification