H2020-MSCA ITN
Grant n. 956099

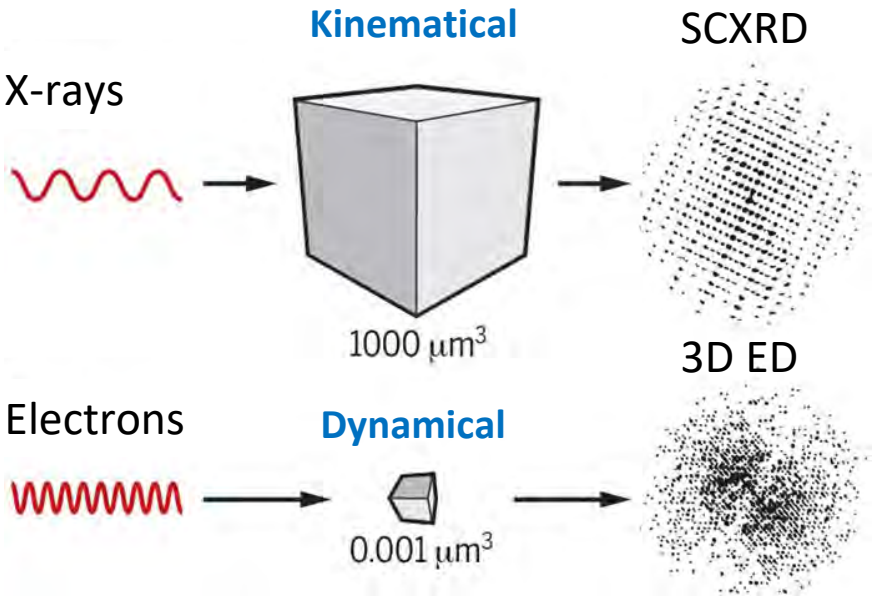
Research Theme 11

Development of serial (rotation) electron diffraction and its application on MOFs and pharmaceutics

Angelina Vypritskaia – Stockholm University

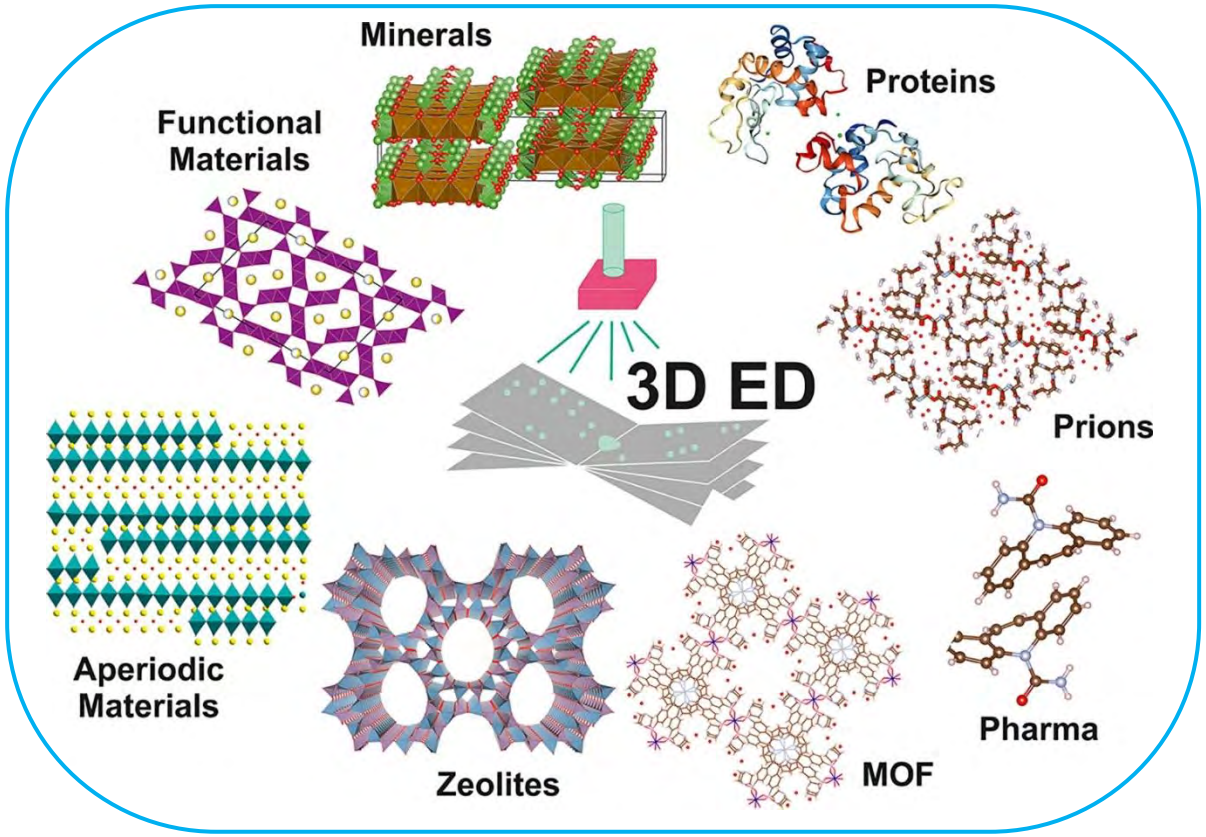
Phase analysis and structure determination of polycrystalline materials

3D electron diffraction (3D ED)



Electrons interact much stronger with atoms
3D ED can handle crystals with sizes ≥ 50 nm

Applications



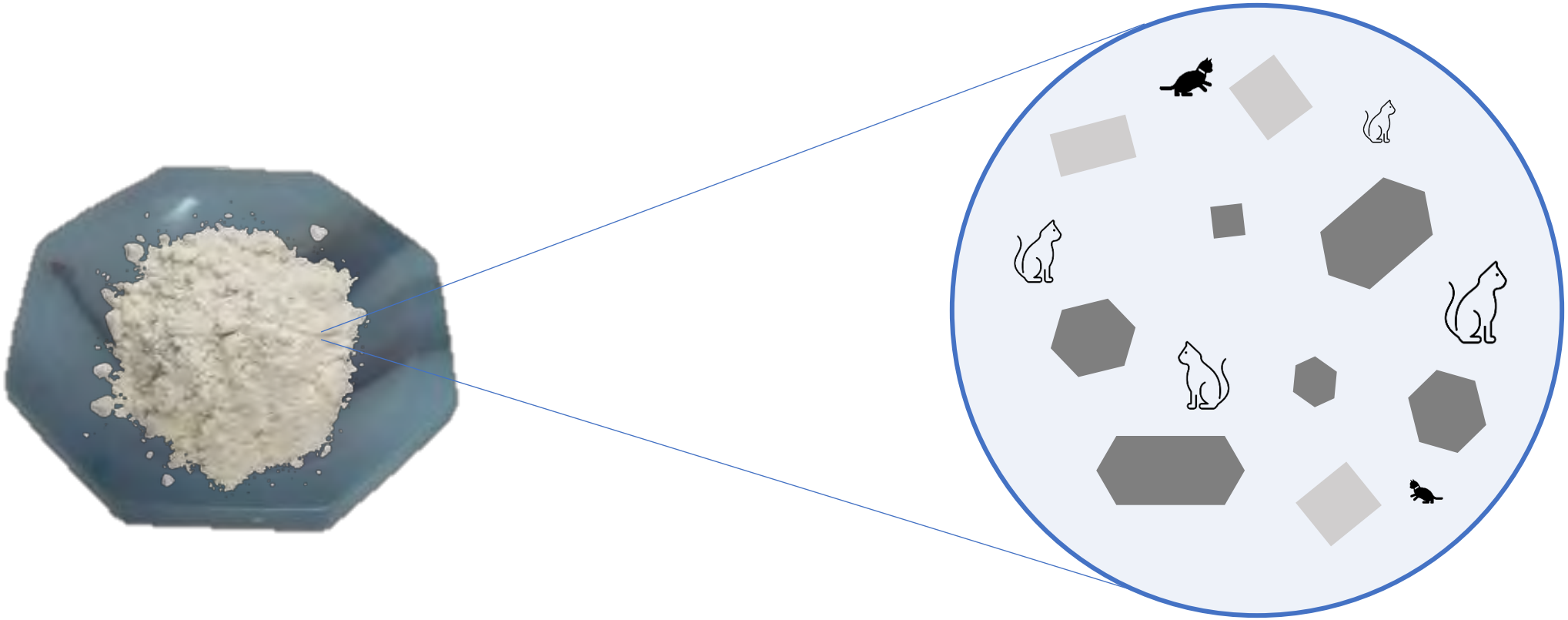
M. Gemmi , X. Zou, S. Hovmöller, A. Migliori, *et. al*., Acta Crystallogr., Sect. A, **2003**. 59, 117-126

D. Zhang, S. Hovmöller, P. Oleynikov, and X. Zou, Z. Kristallogr., **2010**, 225, 94-102

L. B. McCusker, *Science*, **2017**, 355(6321), 136.

M. Gemmi, E. Mugnaioli, T. E. Gorelik, U. Kol, L. Palatinus, P. Boullay, S. Hovmöller, and J. P. Abrahams, *ACS Cent. Sci.* **2019**, 5(8),1315-1329.

How many phases in one powder?

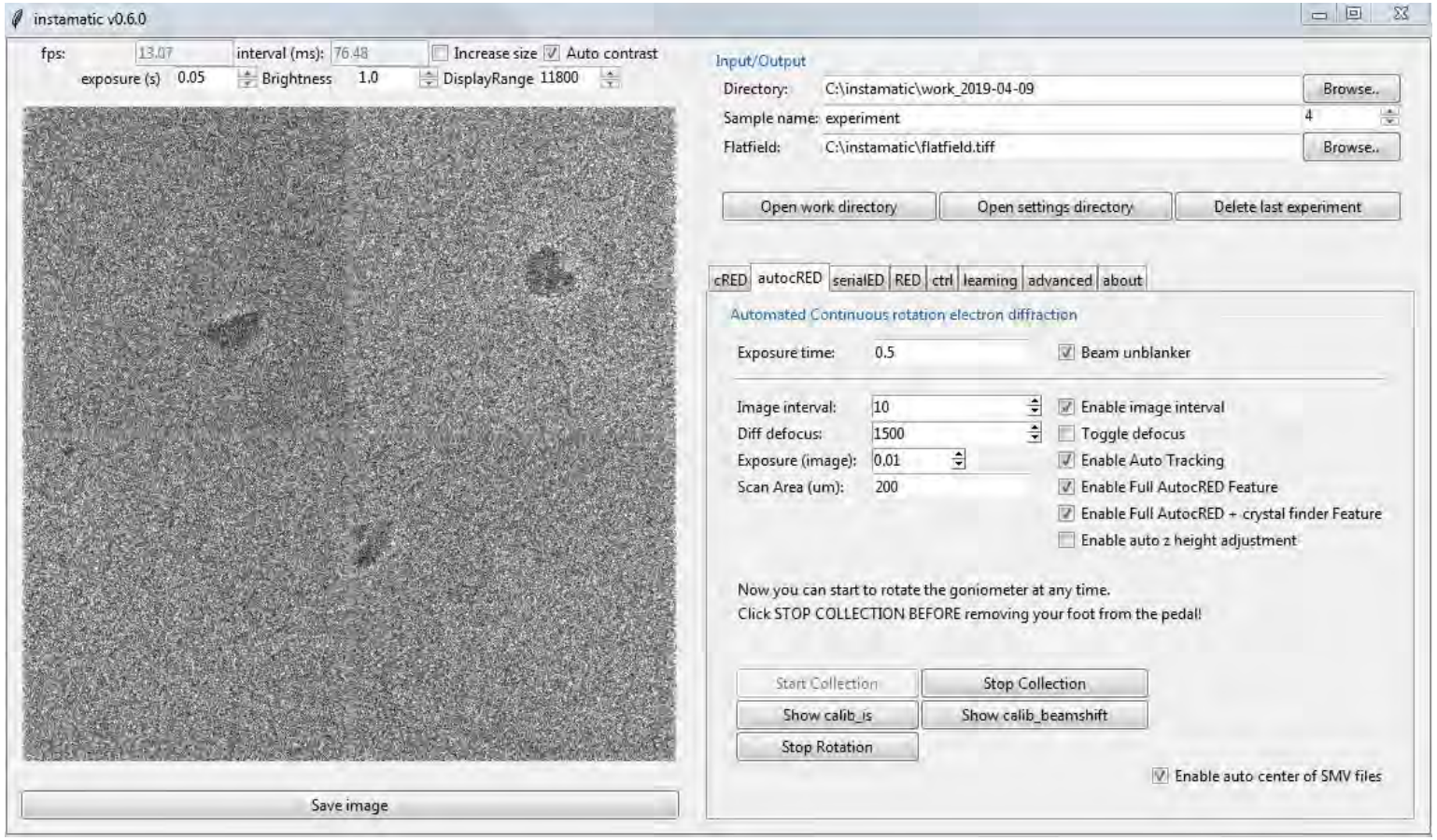


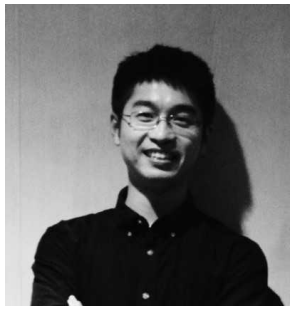
How can we find all the phases?

We can analyse many different crystals

Serial rotation electron diffraction (SerialRED)

Combine reliable phase analysis and structure determination in a single technique





Bin Wang

Stef Smeets

Automatically examine a large number of crystals and collect 3D ED data

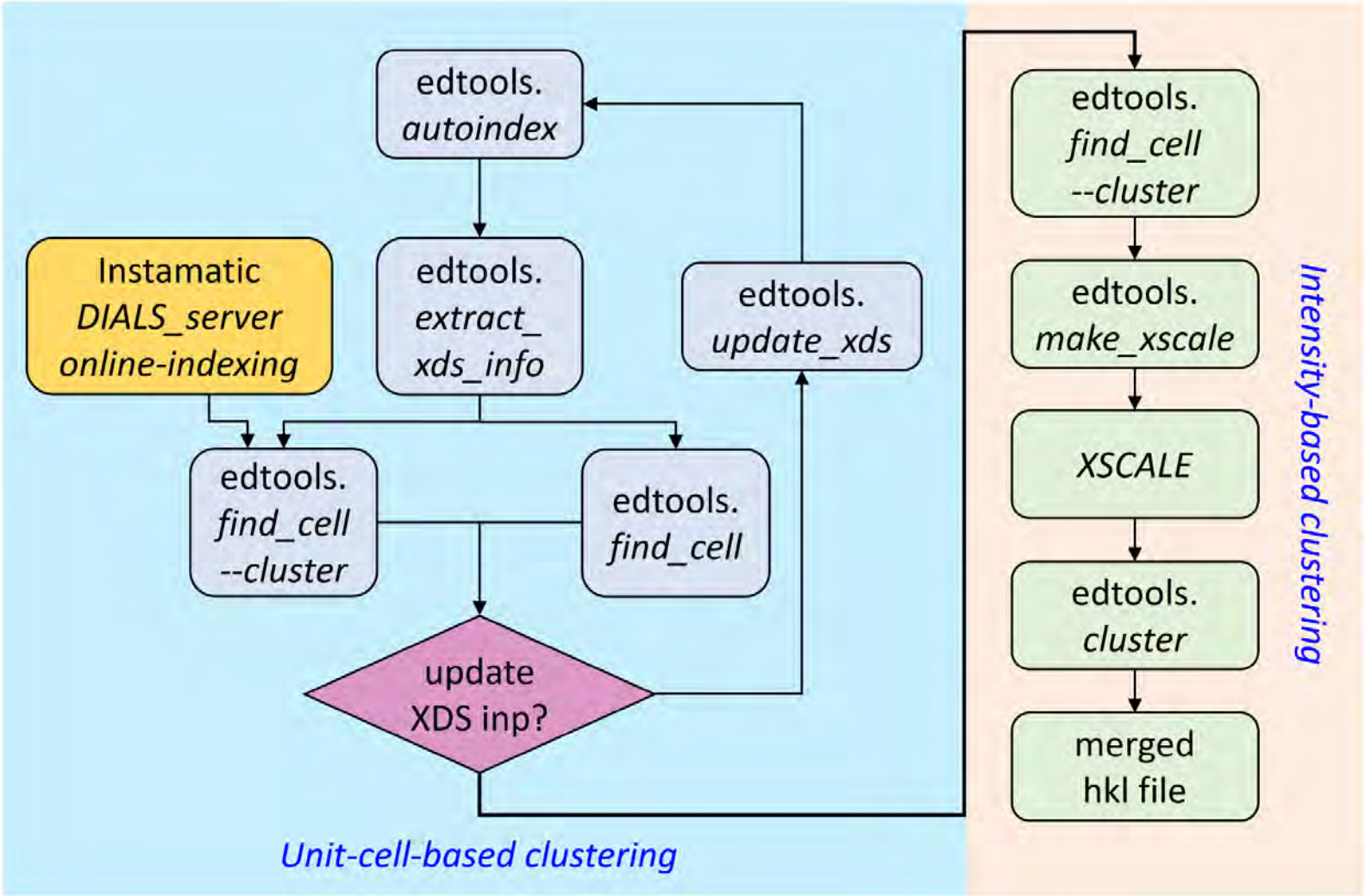
High-throughput phase analysis and structure determination

Typical data collection screens up to 500 crystals/hour

B. Wang, X. Zou, S. Smeets, *IUCrJ* , **2019**, 6, 854-867

SerialRED data processing

Data processing workflow using *edtools*



Exploring complex zeolite products using SerialRED

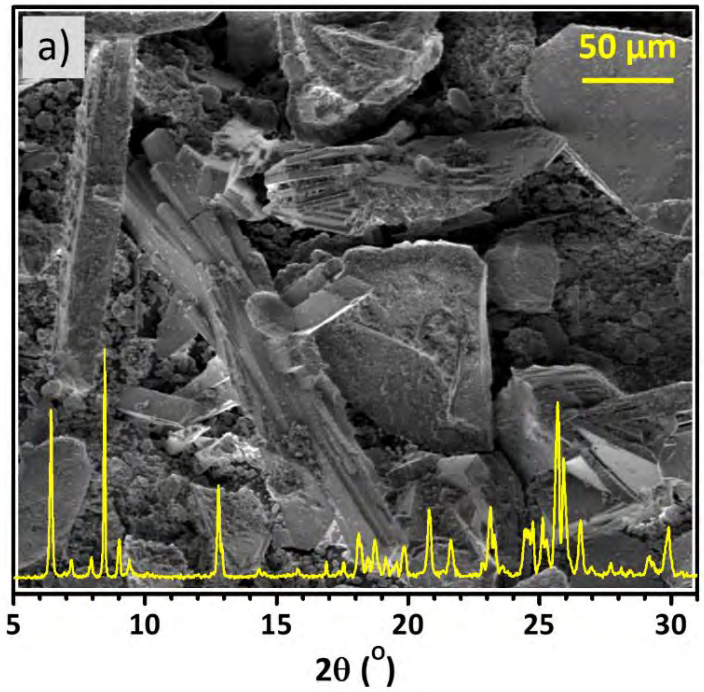
A complex synthesis system was designed for synthesizing novel zeolites

Synthesis parameters and phase diagram

OSDA/Si=0.6, HF/Si=0.6, H_2O/Si=10				
		Si/Ge		
		15	10	5
(Si+Ge)/T^{III} =∞		TON	TON+POS	POS
(Si+Ge)/Al	100	NON	Amor. +Den.+*UOE	Amor.+Den.+*UOE
	20	Amor.	Amor. +RTH+IWV+*CTH	RTH+*UOE+POS+IWV+*CTH
	15	Amor.+Den.+*UOE+IWV	Den.+RTH+*UOE+POS+IWV+*CTH	RTH+*UOE+POS+IWV+*CTH
	10	RTH	RTH+*UOE+POS+IWV+*CTH	RTH+IWV+*CTH
	5	Amor.	Amor.	RTH
(Si+Ge)/B	100	NON	Amor.	Amor.+POS
	20	Amor.+SFE	SFE	SFE+TON
	15	Amor.+SFE	SFE	SFE+TON
	10	SFE	SFE	SFE
	5	SFE	SFE	SFE

The synthesis experiments were performed 7 years ago (2015)
Many complex mixtures

A typical mixture: Product A



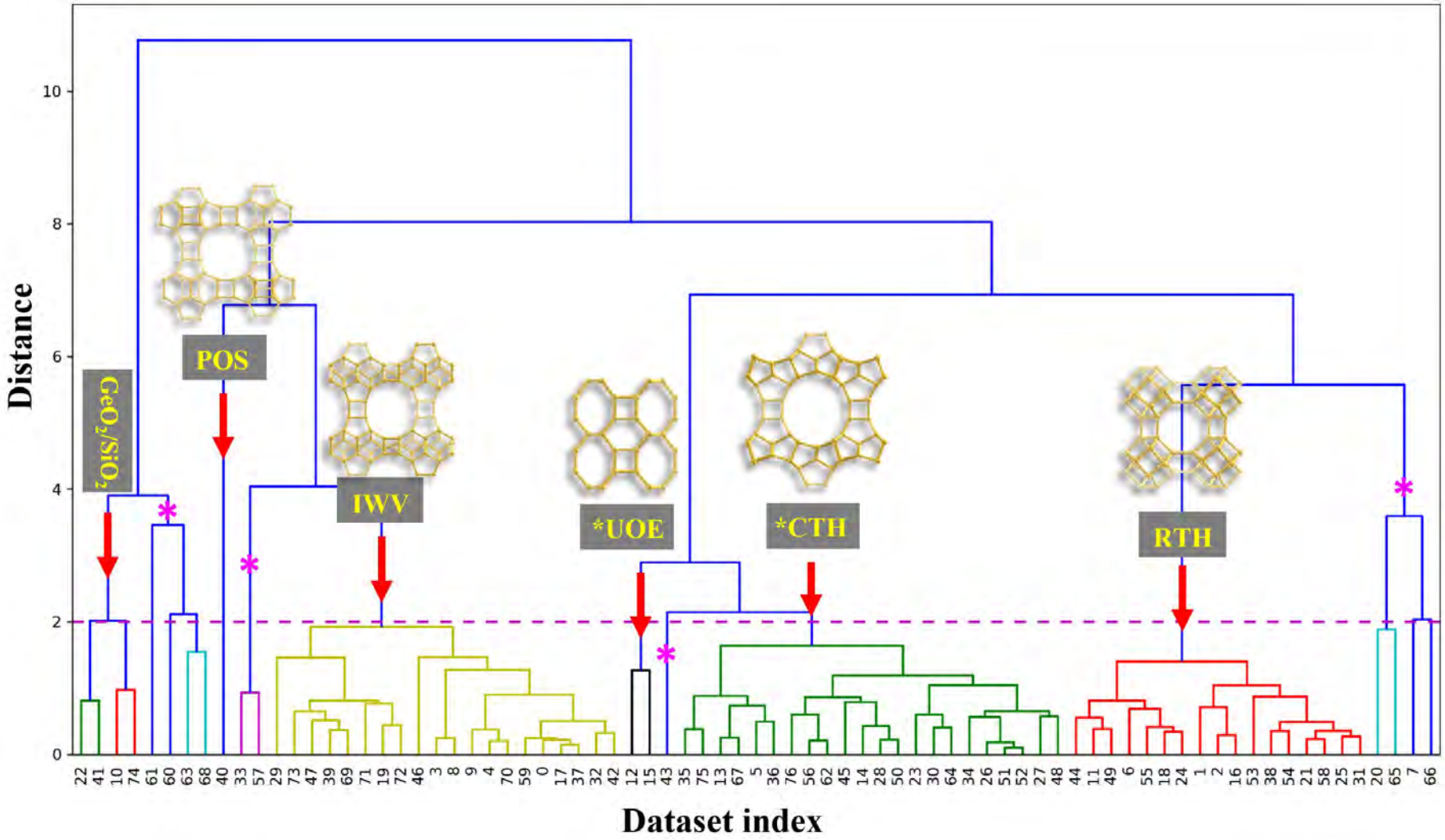
Needle- and plate-like crystals

Two phases?

Y. Luo, B. Wang, S. Smeets, W. Yang, X. Zou, ***preprint in ChemRxiv, DOI:*** 10.26434/chemrxiv-2021-34v44

Phase analysis of Product A using SerialRED

Hierarchical clustering (unit-cell-based)



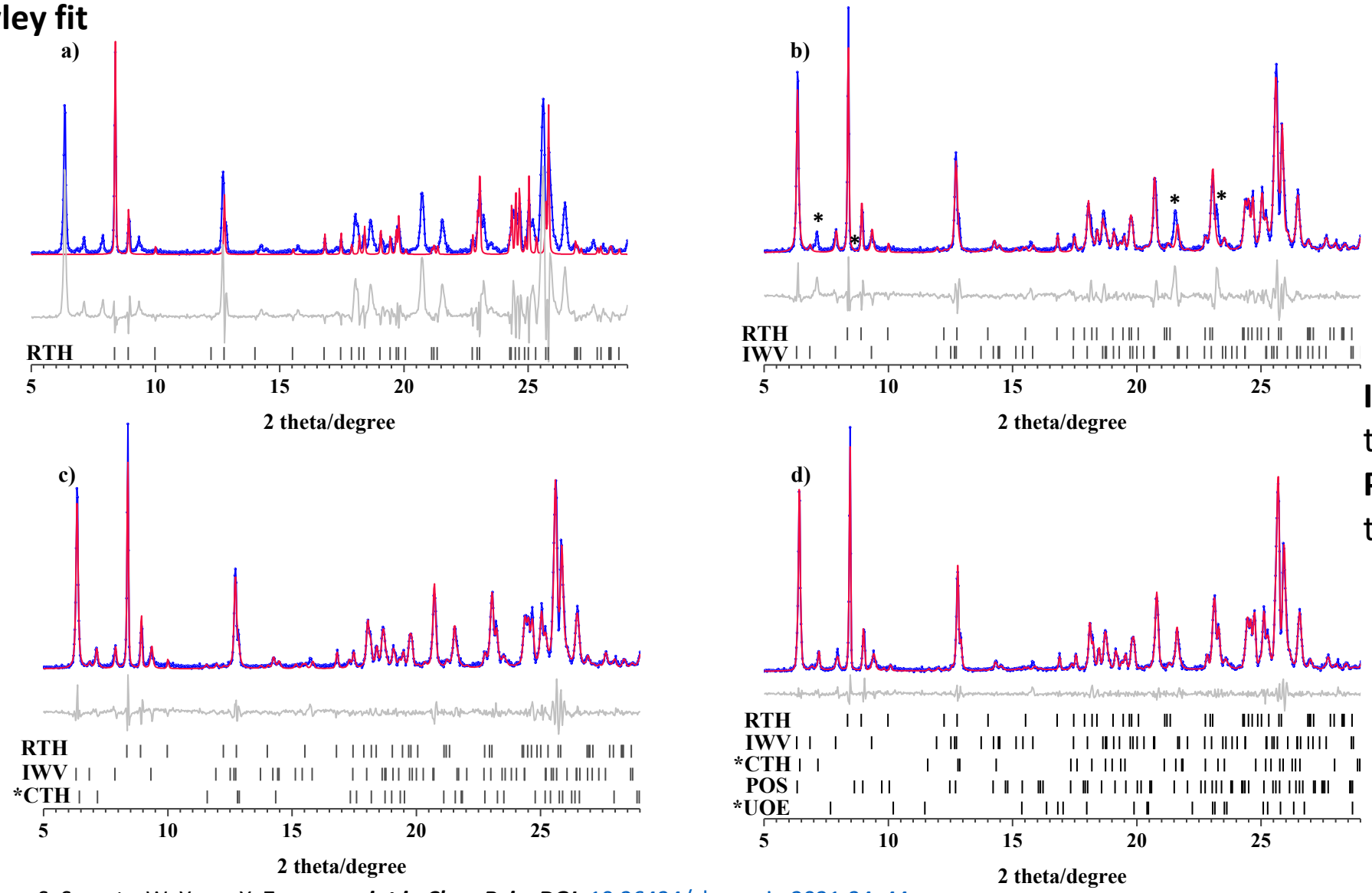
Three more zeolite phases (***CTH**, **POS**, and ***UOE**) were detected.

IWV, **RTH**, ***CTH** could be the major phases, and **POS** and ***UOE** could be the minor phases.

Y. Luo, B. Wang, S. Smeets, W. Yang, X. Zou, ***preprint in ChemRxiv, DOI:*** 10.26434/chemrxiv-2021-34v44

Phase analysis of Product A using PXRD

Pawley fit



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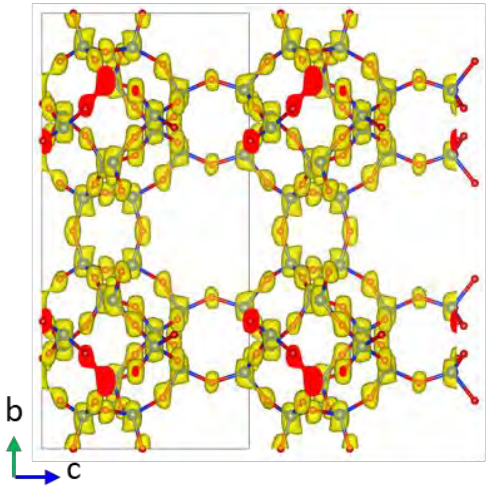
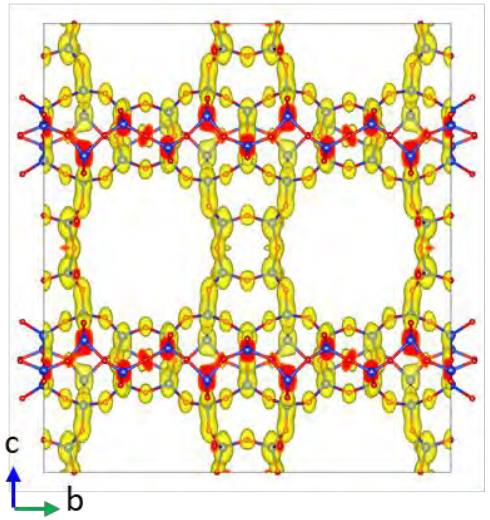
Y. Luo, B. Wang, S. Smeets, W. Yang, X. Zou, ***preprint in ChemRxiv, DOI:*** 10.26434/chemrxiv-2021-34v44

SerialRED: reveal phase and structural infromation for rational synthesis

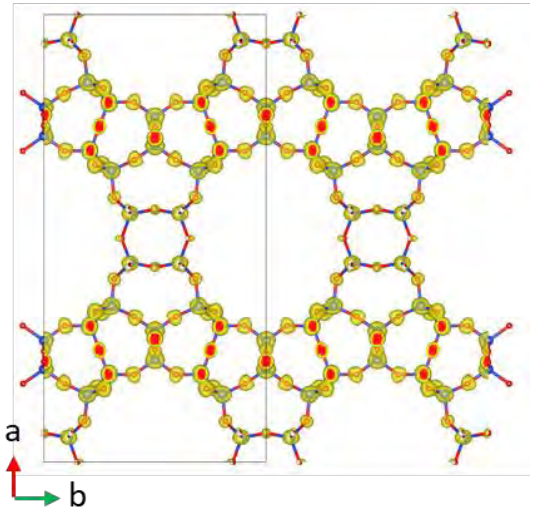
RTH



IWV



***CTH**

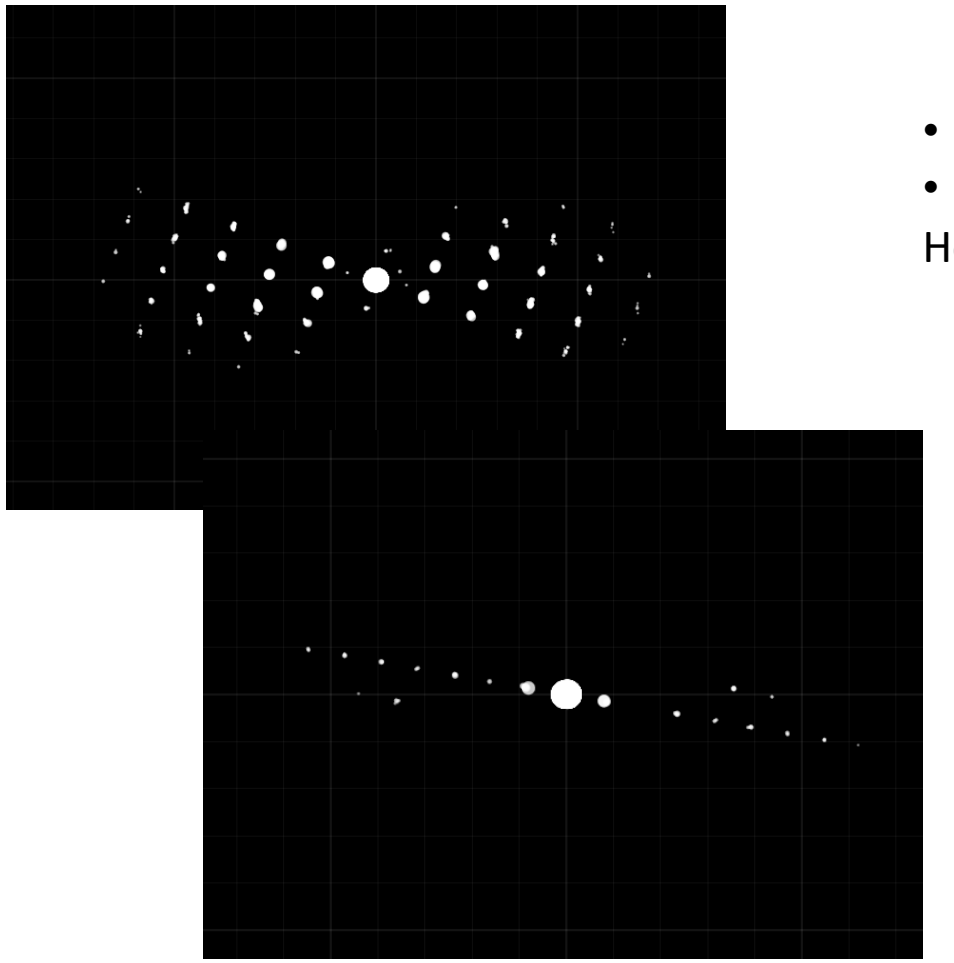


- Structural relationships
- Roles of different T atoms

Phase	**RTH**	**IWV**	***CTH**
Unit cell (Å)	9.68, 20.83, 10.00, β=95.4˚	27.83, 26.08, 13.94	13.69, 27.50, 5.04
Space group	$C2/m$	$Fmmm$	$Cmm2$
Resolution (Å)	1.0	0.8	0.8
Completeness (%)	52.0 (merged 5 data sets)	97.6 (merged 8 data sets)	79.9 (merged 5 data sets)
$R_{int}/R_1/wR_2$	0.1238/ 0.2736/ 0.6111	0.2908/ 0.3165/ 0.6678	0.1375/ 0.2165/ 0.5162
Refection(observed)	624 (397)	2549 (1202)	1565 (1135)
Parameters (restraints)	113 (108)	153 (218)	69 (25)

Y. Luo, B. Wang, S. Smeets, W. Yang, X. Zou, ***preprint in ChemRxiv, DOI:*** 10.26434/chemrxiv-2021-34v44

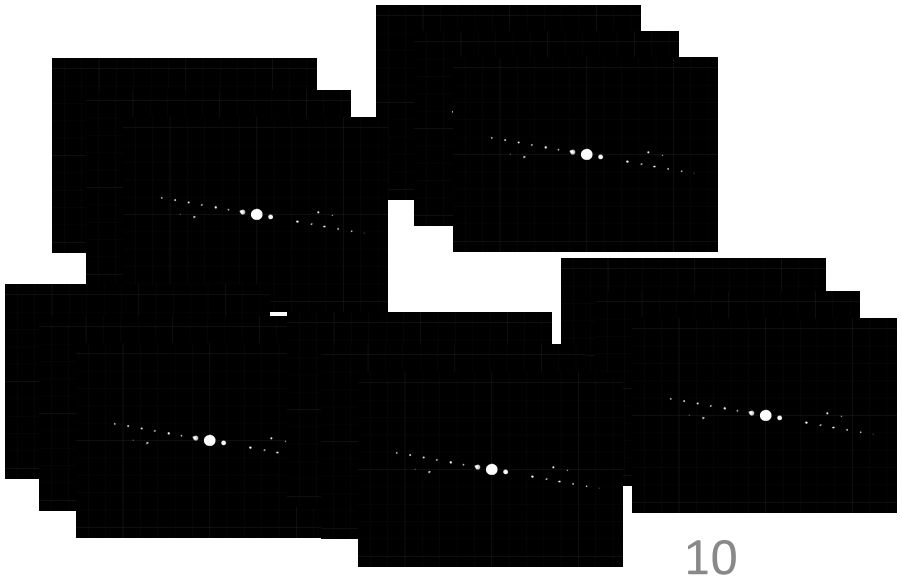
Sensitive samples



- Too sensitive to get good data
- Intensities can be wrong

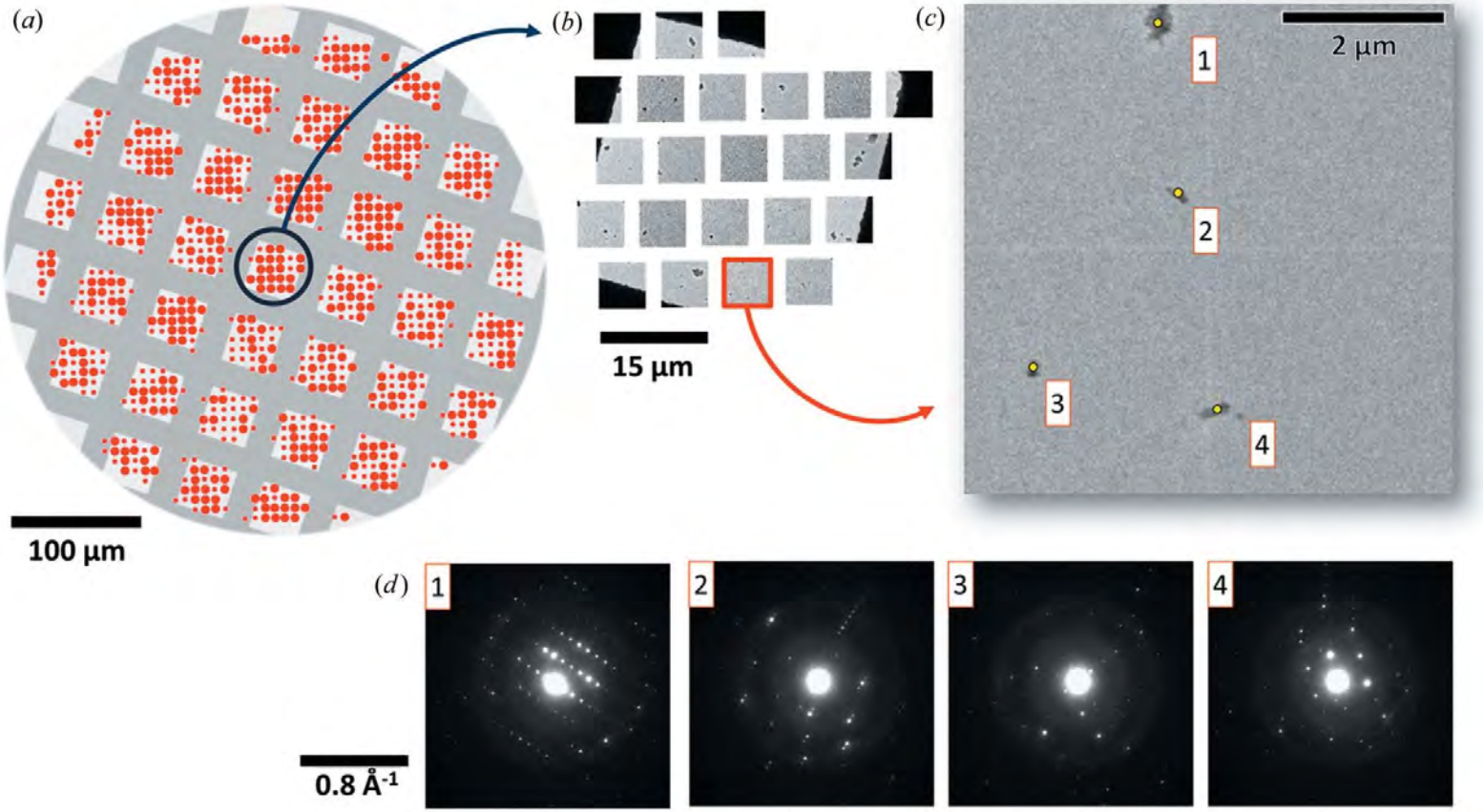
How can we solve the structure?

Get data from more crystals!



Serial electron diffraction (SerialED)

TEM mode



Stef Smeets

Automatically identify crystals and collect ED data

Short exposure time (0.05s/frame)

Examine a large number of crystals (3500 crystals/hour)

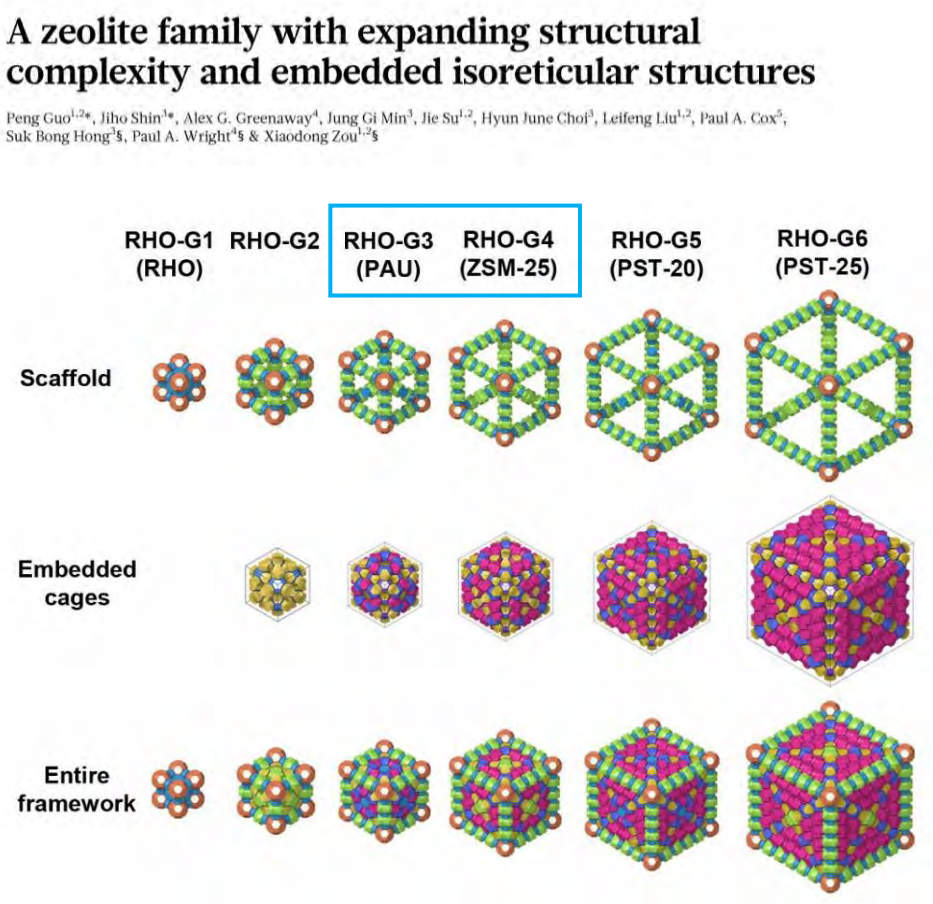
high quality ED data on electron beam sensitive materials for structure determination

high-throughput phase analysis

S. Smeets, X. Zou, W. Wan, *J. Appl. Cryst.*, **2018**, 51, 1262-1273

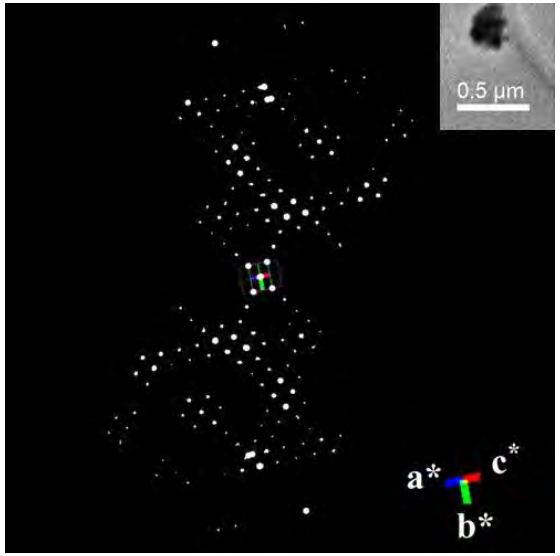
Ab initio structure determination of polycrystalline materials using SerialED

Electron beam sensitive zeolite ZSM-25

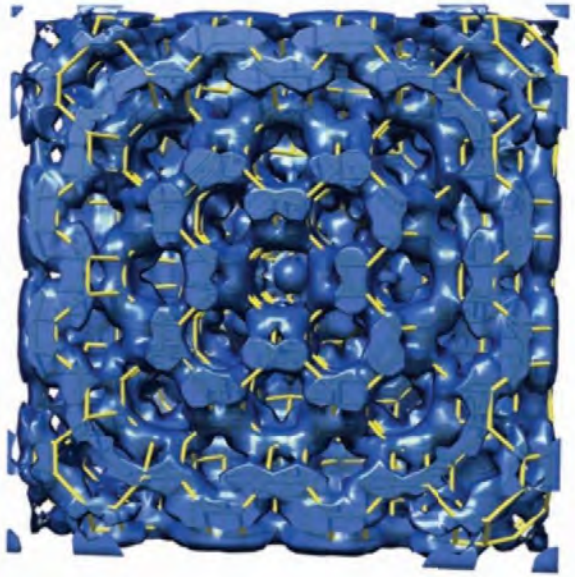


Nature, **2015**, 524, 74-78

RED data, resolution **2.5 Å**



Structure solution:
RED strong reflections +
calculated phases from **PAU**



Symmetry: *Im*-3*m*

Limitations

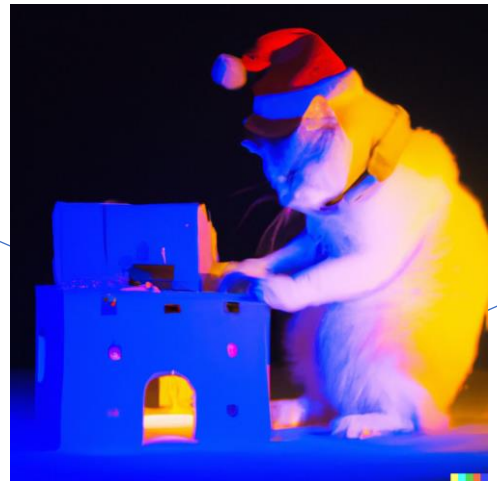
- Not great crystal recognition

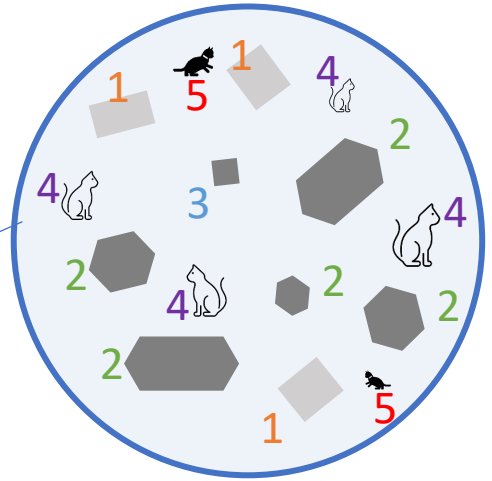
  Algorithm can take Cu grid as a crystal

- No differentiation by phases

→ machine learning algorithm to recognise crystals

→ algorithm to recognise phases by shape



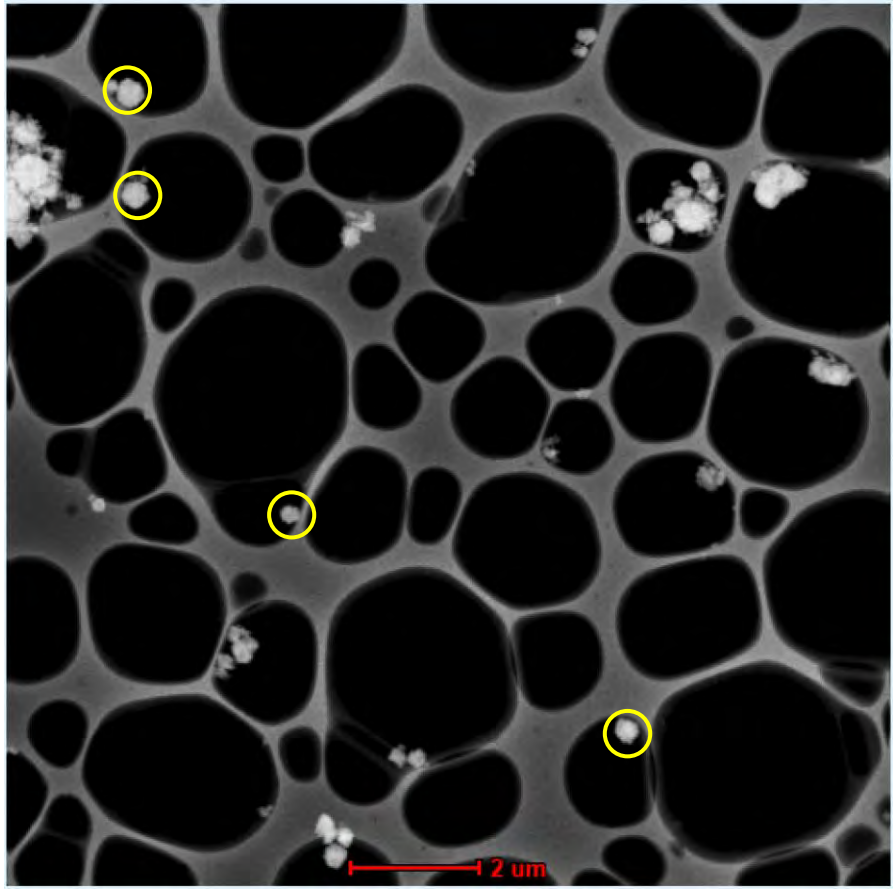


Thank you for the attention!

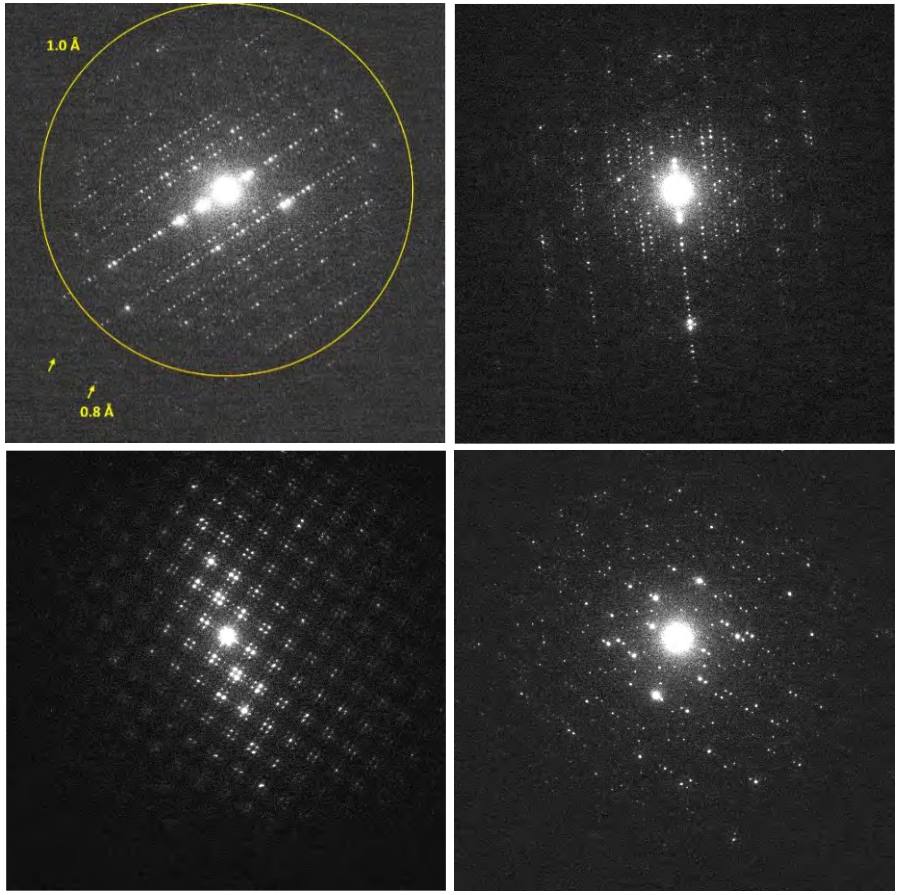
Ab initio structure determination of polycrystalline materials using SerialED

SerialED data of as-made ZSM-25

Map of the crystals



Selected patterns from serialED data



Resolution: **0.80 Å**

(RED: 2.5 Å)

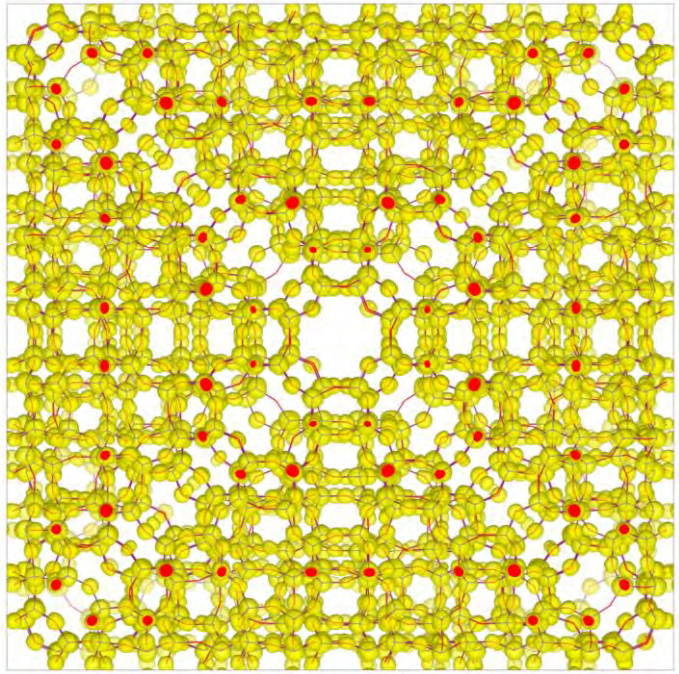
Completeness: 100%

P. Hogan-Lamarre, Y. Luo, R. Bücker, R. J. D. Miller, and X. Zou, ***In manuscript***

Ab initio structure determination of polycrystalline materials using SerialED

Structure of ZSM-25 determined by SerialED

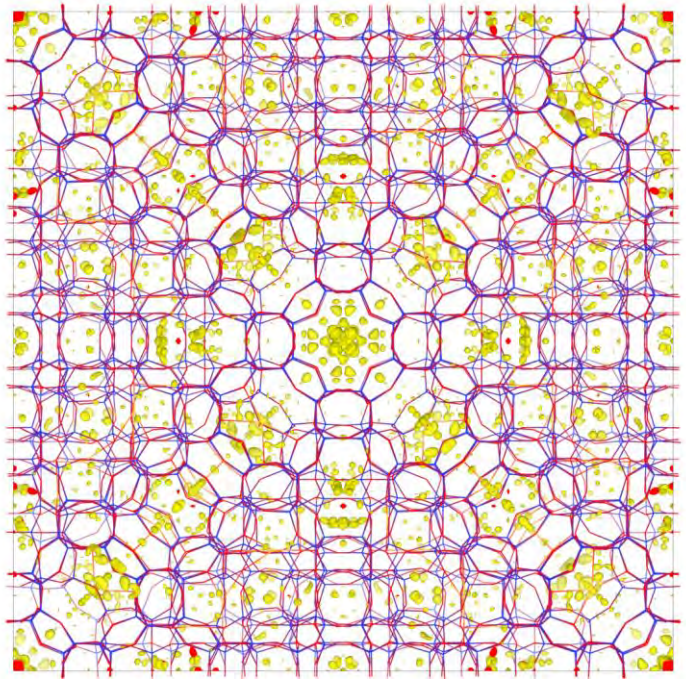
Framework structure: *ab initio* solved



Isosurface level: 0.89 e/Å^3

Resolved all the framework atoms

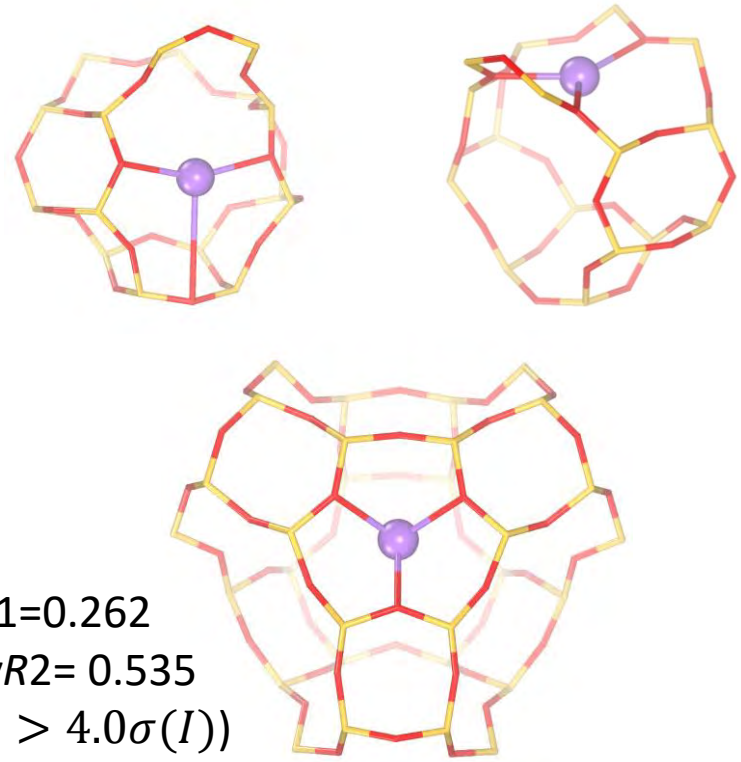
Electron potential difference map



Isosurface level: 0.51 e/Å^3

guest species (OSDAs, H_2O, Na^+)?

Locations of Na^+ cations



*R*1=0.262
*wR*2= 0.535
($I > 4.0\sigma(I)$)

Understand the roles of cations

P. H. Lamarre, Y. Luo, R. Bücker, X. Zou, et al., ***unpublished***