

ECM-28, Warwick, UK
29-08-2013

ETH zürich

USING *FOCUS* AND *SUPERFLIP* TO SOLVE STRUCTURES FROM 3D ELECTRON AND POWDER DIFFRACTION DATA

Stef Smeets

Laboratory for Crystallography

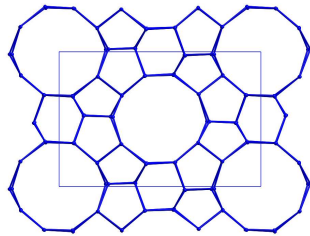
ETH Zürich, Switzerland

Outline

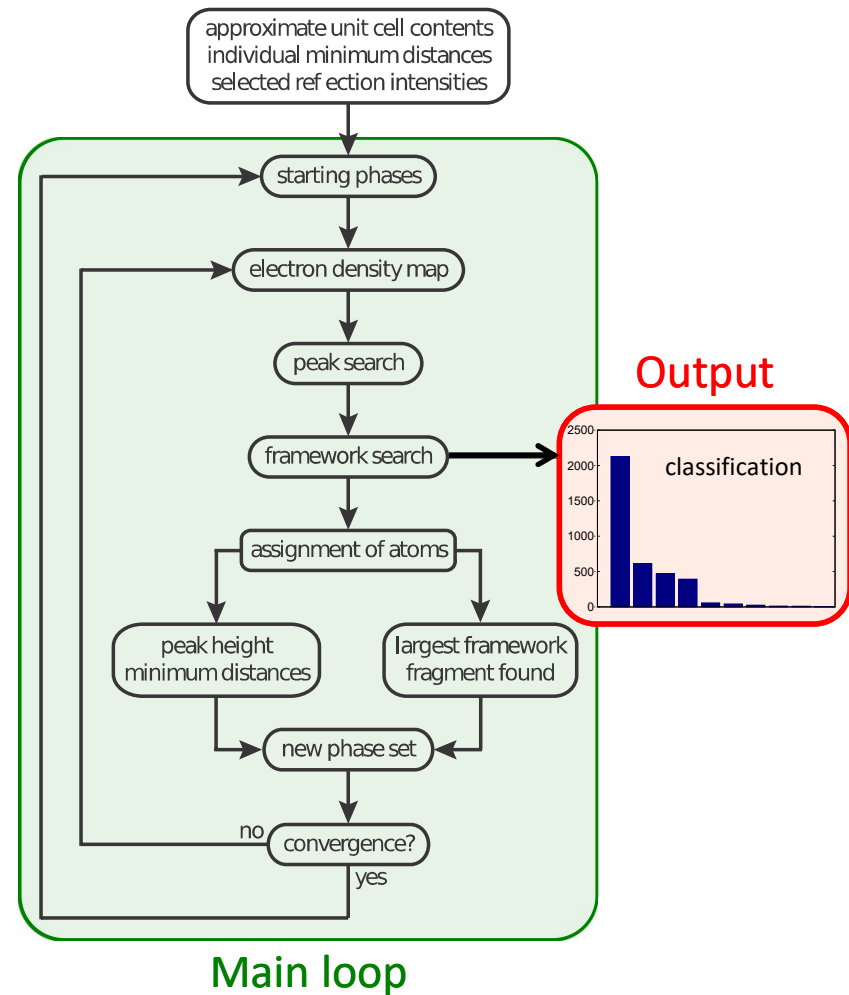
- Part I: Application of FOCUS to ED data
 - FOCUS
 - Application to 5 zeolite samples
- Part II: Combining ED and XRPD data
 - Full pattern (p)repartitioning
 - FOCUS with combined data
 - Charge flipping with combined data set
- Conclusions

FOCUS

- Dual-space method specific to zeolites
- Zeolite model building
 - 3d-connected frameworks
 - Tetrahedral connectivity
 - Bond distances/angles known



- Framework search
 - Classification of results
- Developed with XRPD data in mind



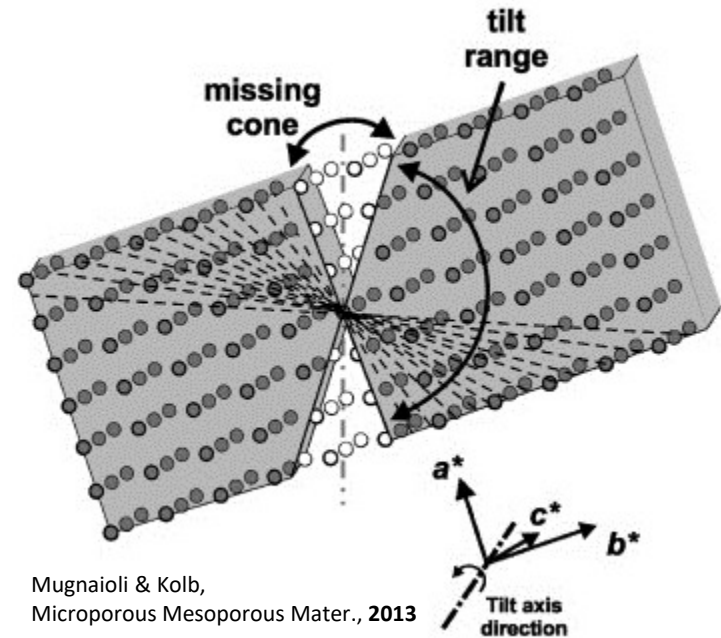
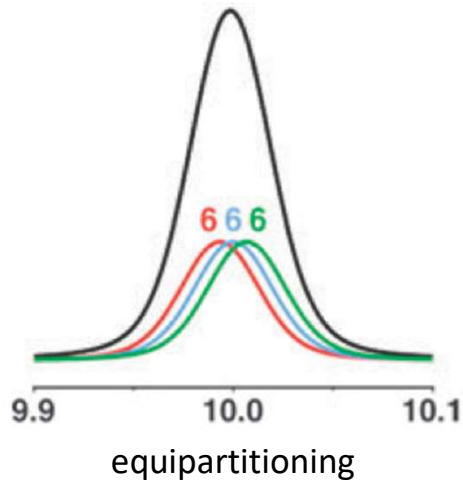
Grosse-Kunstleve *et al.*, *J. Appl. Cryst.*, **1997**

The problem with XRPD/ED...

- XRPD: Overlap
- ED: dynamical scattering, beam damage, low completeness, ...



Result: 'Less than ideal data'



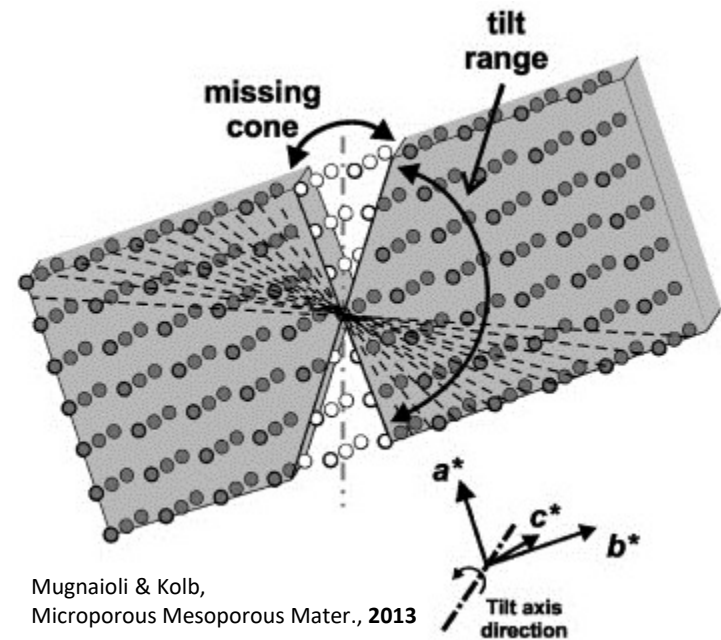
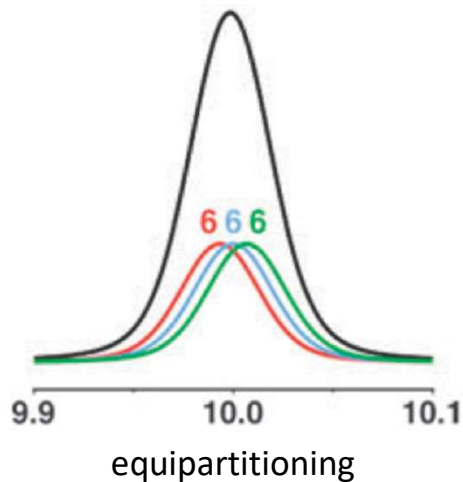
Mugnaioli & Kolb,
Microporous Mesoporous Mater., 2013

	XRPD	ED
Data completeness	100%	40-100%
Reflection intensities	Accurate	Inaccurate
Reflection overlap	Yes	No

The problem with XRPD/ED...

- XRPD: Overlap
- ED: dynamical scattering, beam damage, low completeness, ...

Result: 'Less than ideal data'



Mugnaoli & Kolb,
Microporous Mesoporous Mater., 2013

FOCUS was modified to work with electron diffraction data.

Smeets *et al.*, J. Appl. Cryst., 2013

Samples for FOCUS

- 4 known zeolites of different complexities for testing new approach
- 1 structure solved first from RED (SSZ-45)

Samples for testing

Unknown
structure

Sample	Natrolite	ZSM-5	ITQ-43	IM-5	SSZ-45
Data	ADT	ADT	ADT	ADT	RED
Space group	<i>Fdd2</i>	<i>Pnma</i>	<i>Cmmm</i>	<i>Cmcm</i>	<i>Fm2m</i>
a (Å)	18.293	20.100	26.411	14.209	13.6
b (Å)	18.640	19.924	41.399	57.237	21.7
c (Å)	6.586	13.424	12.839	19.994	35.03
Indep. T-atoms	3	12	11	24	18
% coverage	100	81	98	95	53
First solved	Model building	DM with XRD	Sir2008 ADT	CF XRPD+TEM	FOCUS

ADT: Automated Diffraction Tomography
RED: Rotational Electron Diffraction

ADT data: Mugnaioli & Kolb, *Microporous Mesoporous Mater.*, **2013**
RED data: Dan Xie (Chevron, USA)

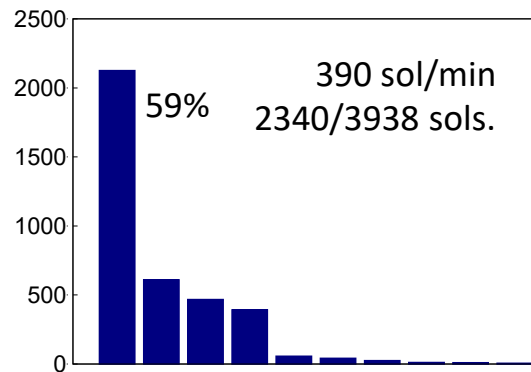
ITQ-43: Jiang, J. *et al.*, *Science*, **2011**

IM-5: Baerlocher *et al.*, *Science*, **2007**

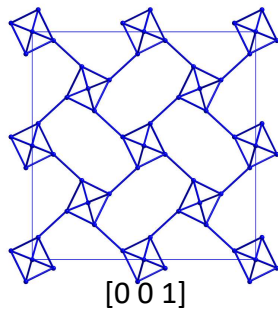
SSZ-45 -> ERS-18: Zanardi *et al.*, *Microporous Mesoporous Mater.*, **2011**

FOCUS with ED data

Natrolite

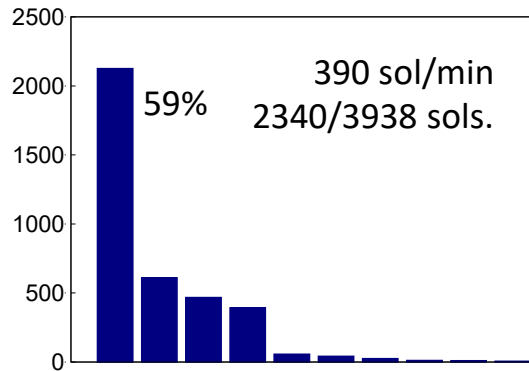


Volume 2245 \AA^3
Indep. T-atoms 3
composition $T_{40}O_{80}$

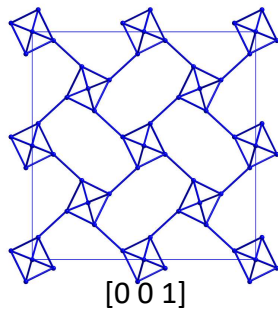


FOCUS with ED data

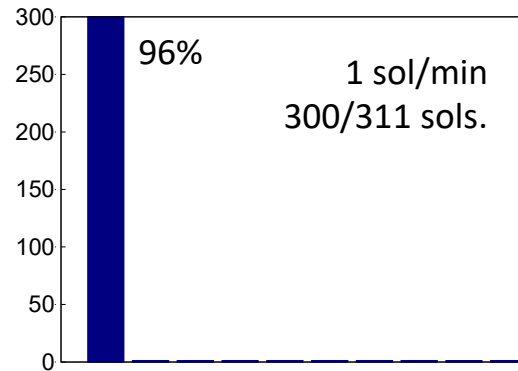
Natrolite



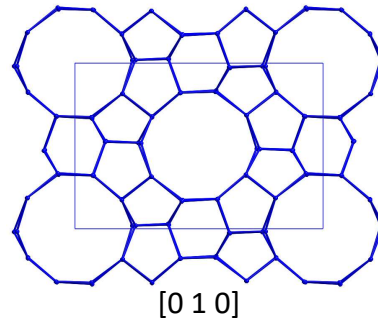
Volume 2245 Å³
Indep. T-atoms 3
composition T₄₀O₈₀



ZSM-5

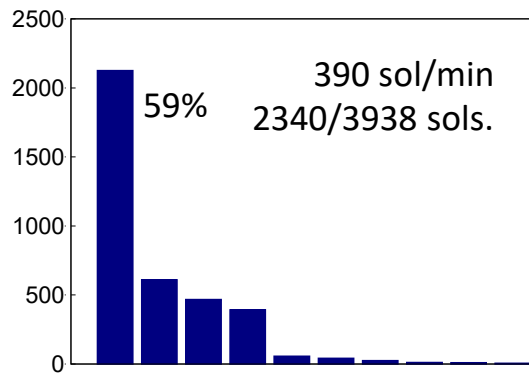


5376 Å³
12
Si₉₆O₁₉₂

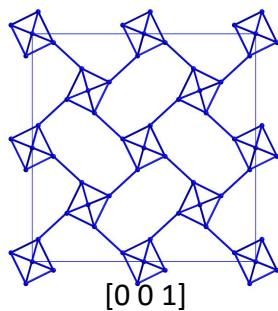


FOCUS with ED data

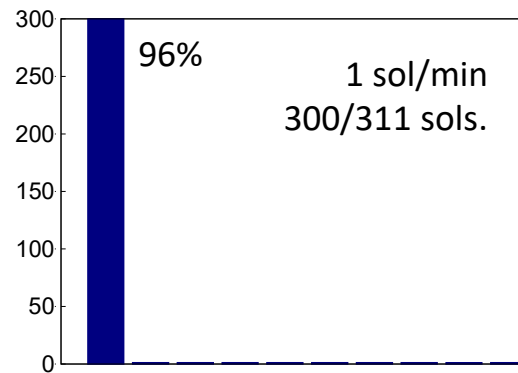
Natrolite



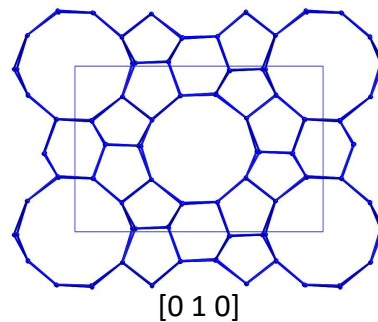
Volume 2245 Å³
 Indep. T-atoms 3
 composition T₄₀O₈₀



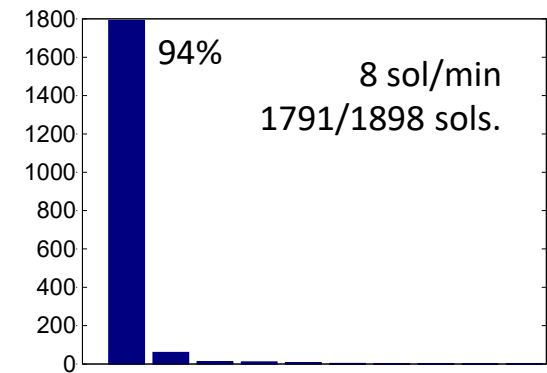
ZSM-5



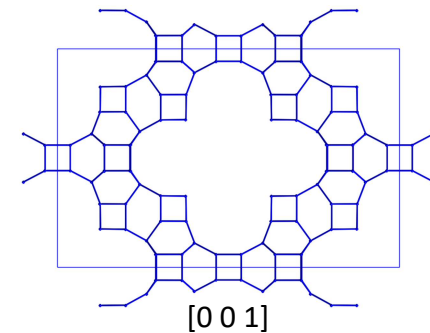
5376 Å³
 12
 Si₉₆O₁₉₂



ITQ-43

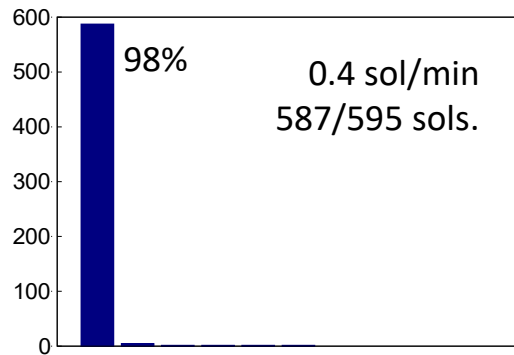


14038 Å³
 11
 T₁₈₀O₃₆₀

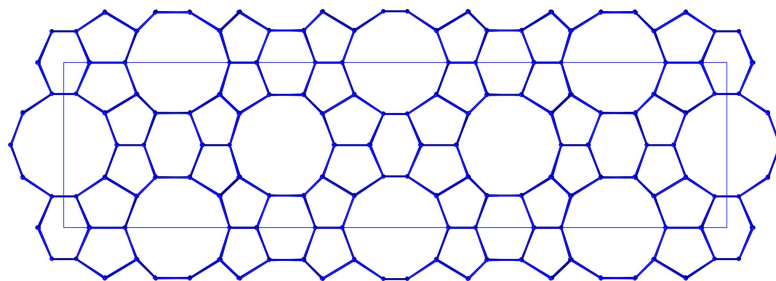


FOCUS with ED data

IM-5



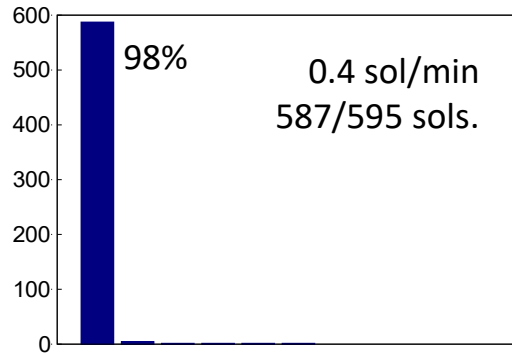
Volume 16260 Å³
Indep. T-atoms 3
composition Si₂₈₈O₅₇₆



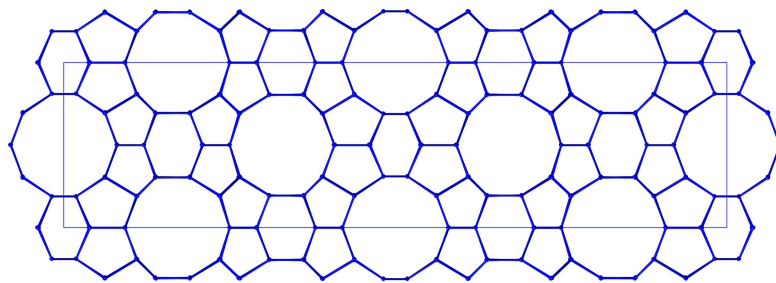
[0 0 1]

FOCUS with ED data

IM-5

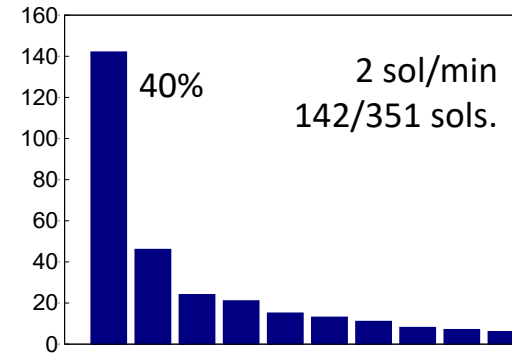


Volume 16260 Å³
 Indep. T-atoms 24
 composition Si₂₈₈O₅₇₆



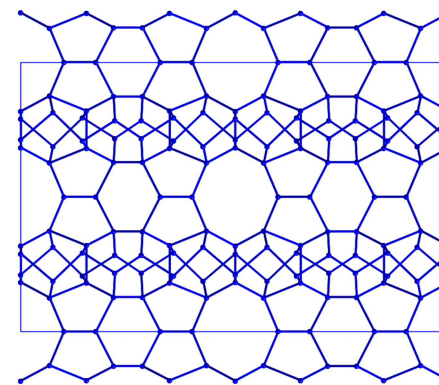
[0 0 1]

SSZ-45



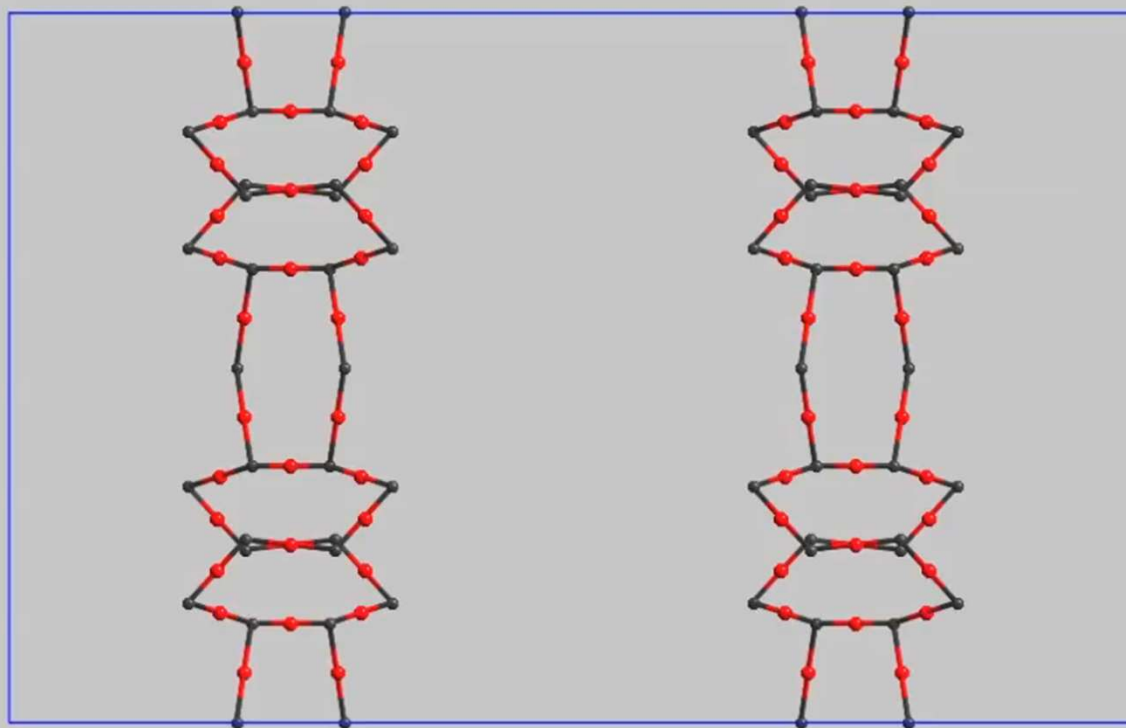
Completeness:
53%

10678 Å³
 18
 Si₂₀₀O₄₀₀



[0 1 0]

SSZ-45 movie

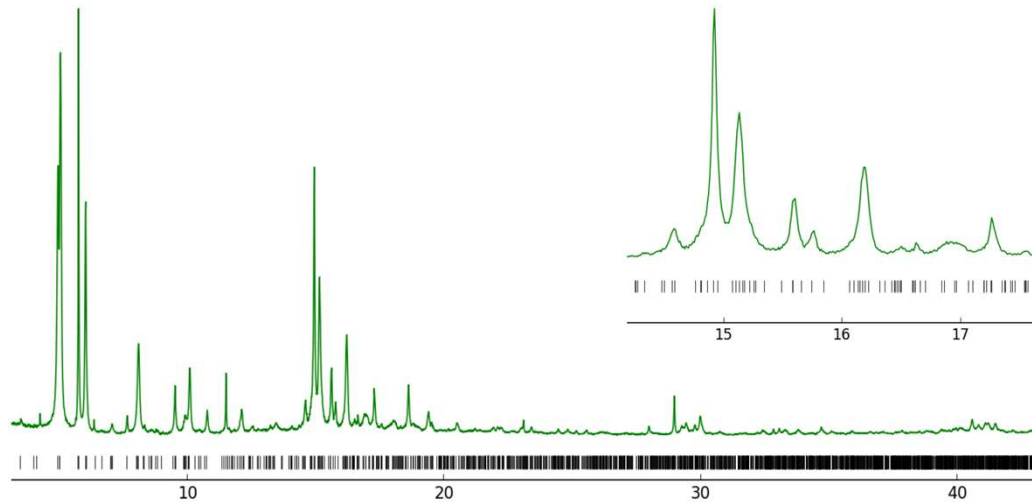


Combining ED and XRPD

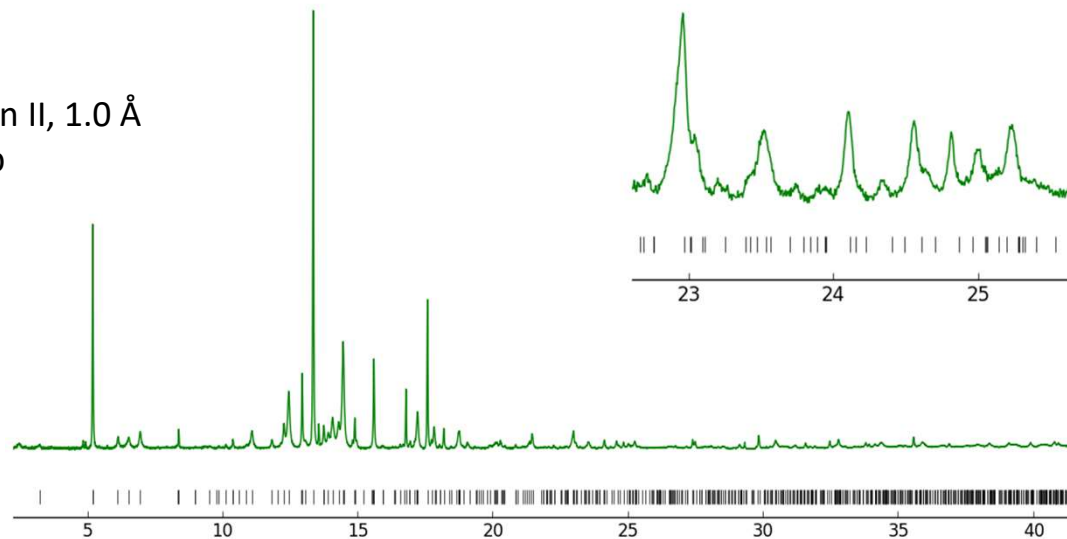
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Combining ED and XRPD

IM-5, SNBL, 0.5 Å
of=0.3, 90% overlap

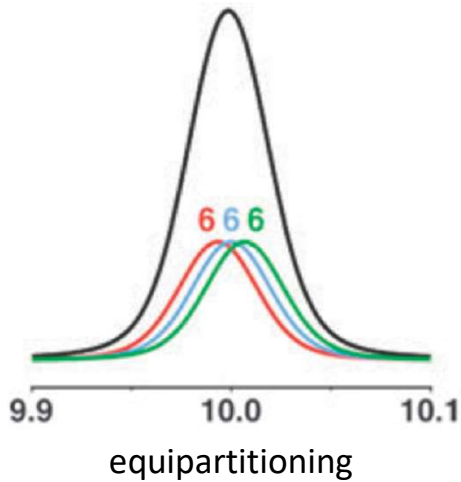
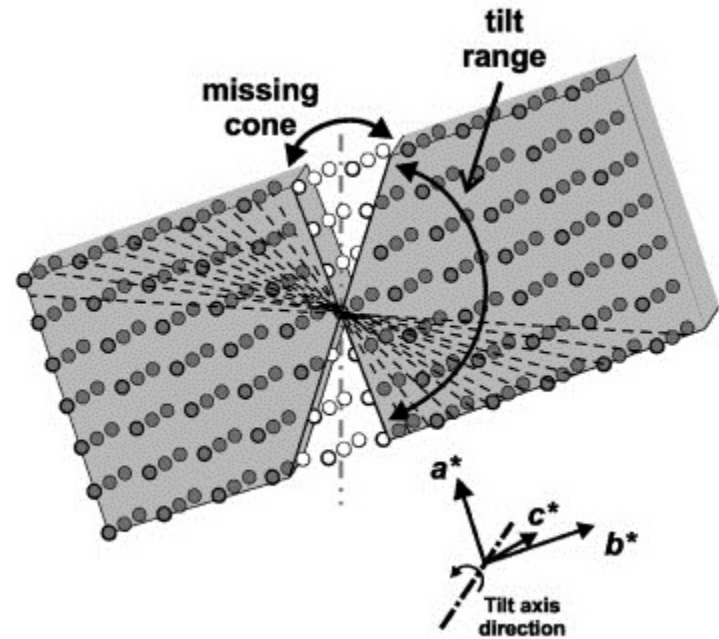


SSZ-45, SLS - Mythen II, 1.0 Å
of=0.3, 80% overlap



Combining ED and XRPD

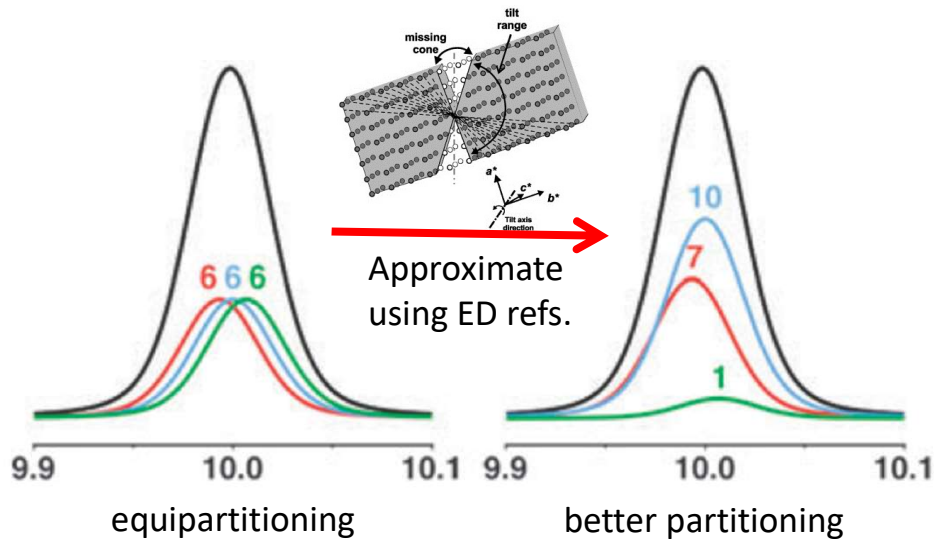
- ED and XRPD have similar problems
 - Data are surprisingly complementary
 - Peak overlap vs. dynamical scattering/beam damage



	XRPD	ED
Data completeness	100%	40-100%
Reflection intensities	Accurate	Inaccurate
Reflection overlap	Yes	No

Full pattern prepartitioning

- Aim: Create a better data set for structure solution than either ED or XRPD
- Pragmatic approach, fully automatic procedure



XRPD:

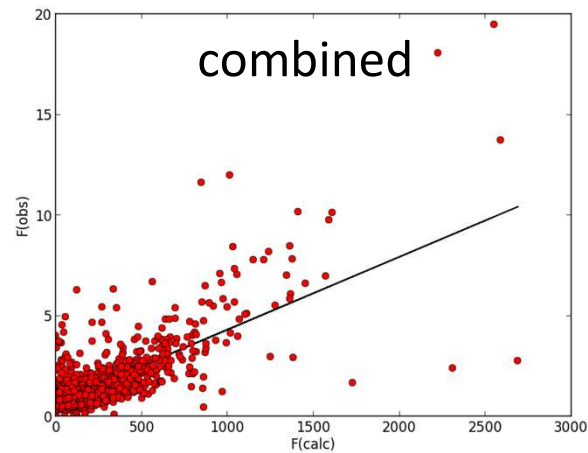
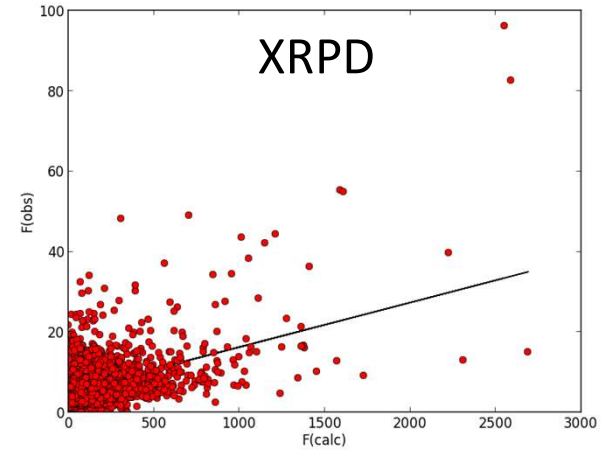
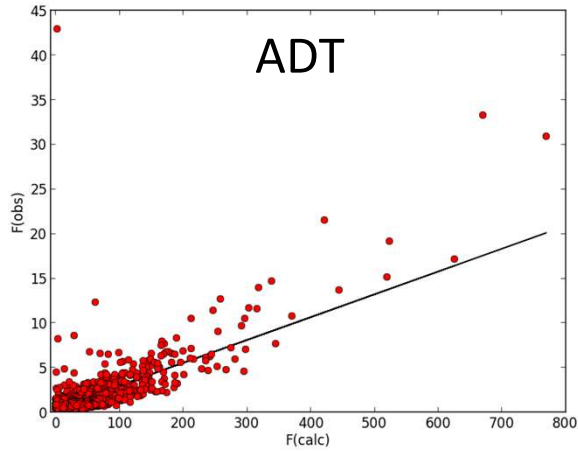
- Accurate total intensity
- Assign reflections to overlap groups

ED:

- Ratio between intensities
- Missing reflections??

Resulting data set can be treated as single crystal XRD

Fobs vs. Fcalc for IM-5

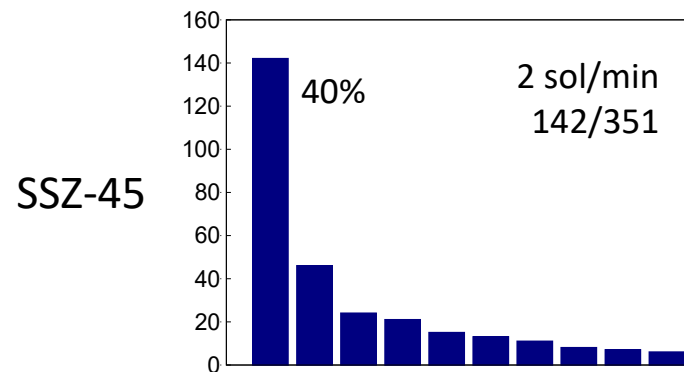
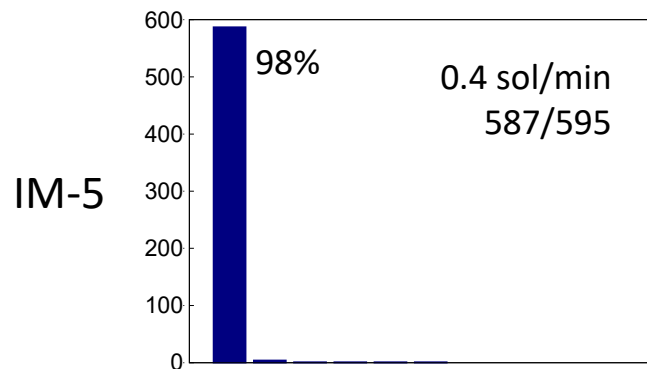


FOCUS with combined data

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 - **FOCUS with combined data**
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FOCUS with combined data

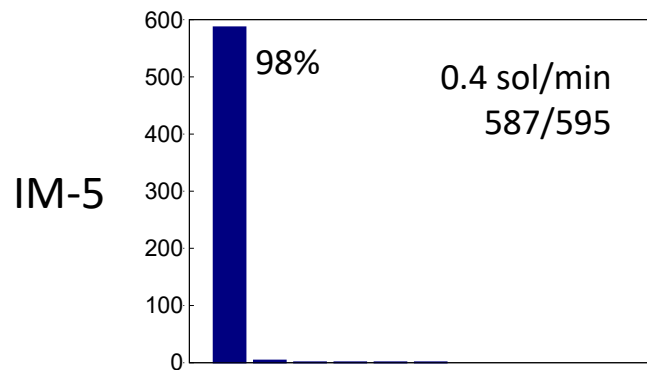
ADT/RED



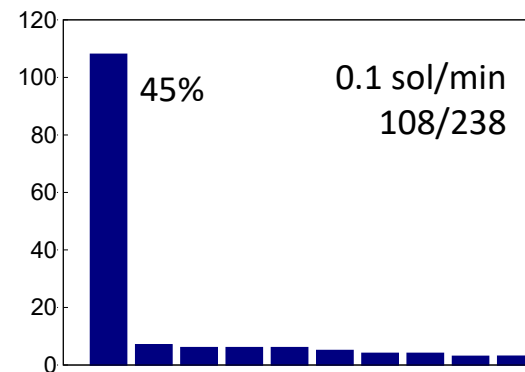
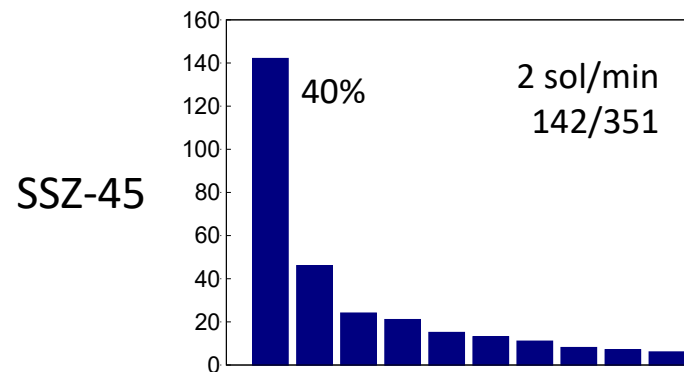
FOCUS with combined data

ADT/RED

XRPD

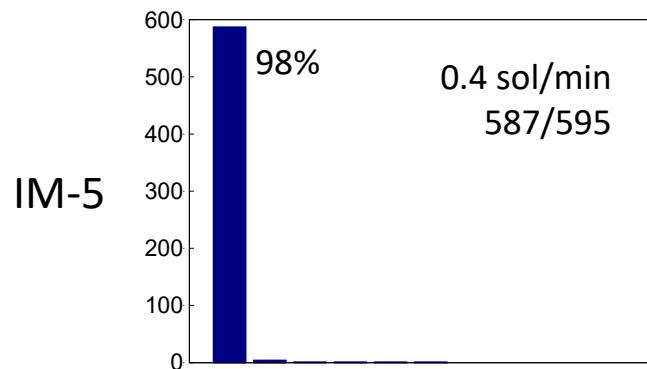


XRPD data cannot be solved with FOCUS



FOCUS with combined data

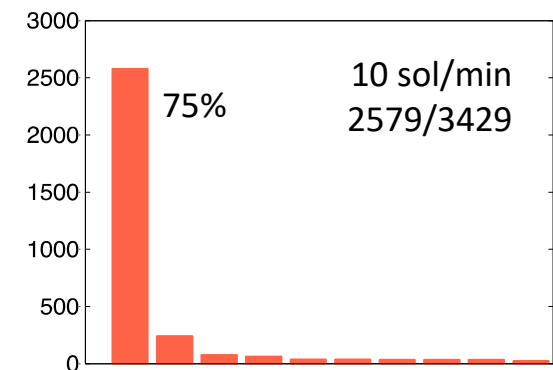
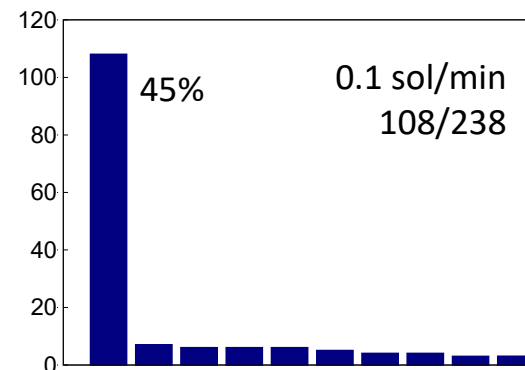
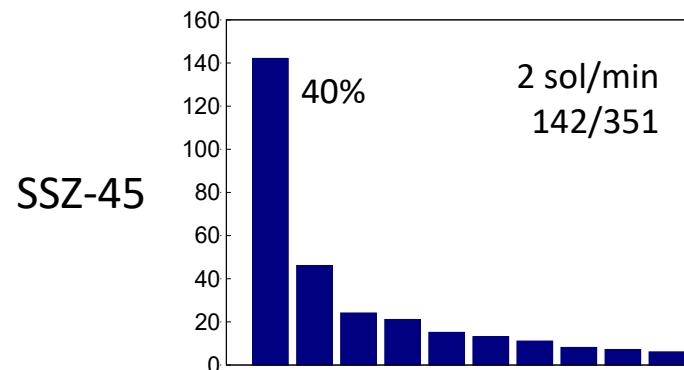
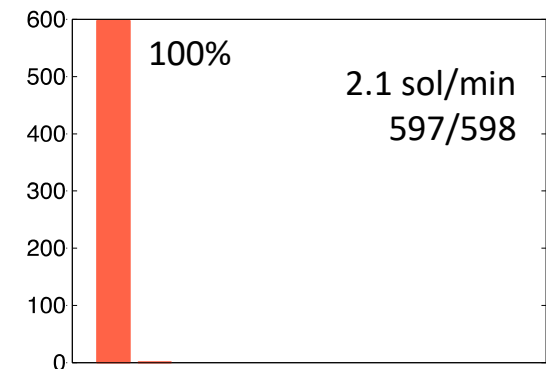
ADT/RED



XRPD

XRPD data cannot be solved with FOCUS

Combined

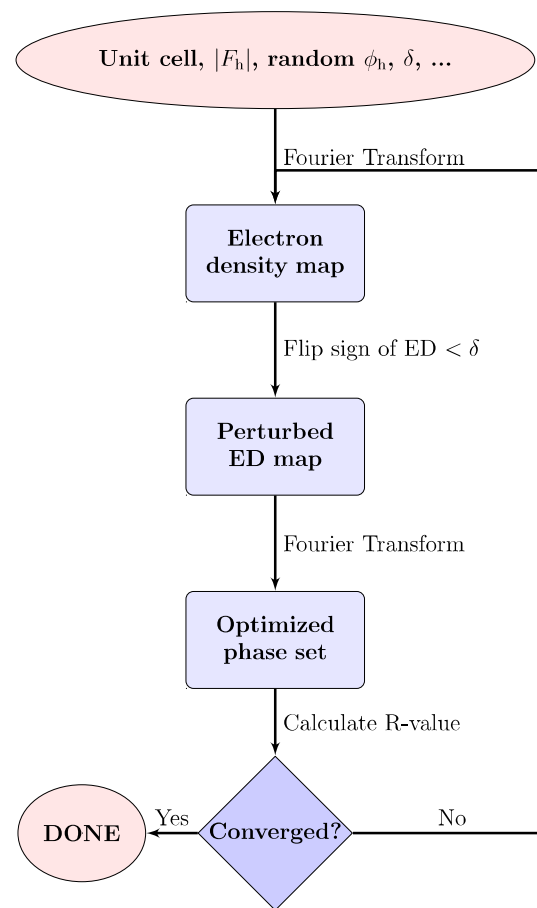


Charge flipping with combined data

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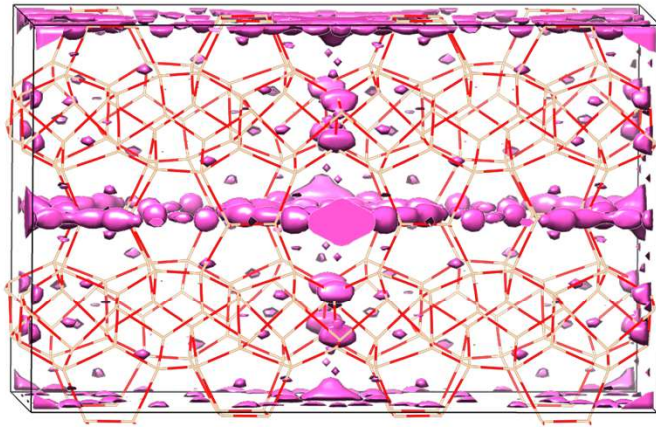
Charge flipping

- Dual space, *ab initio* method
 - No prior knowledge of structure is required
 - General applicable, not limited to zeolites
- Algorithm is deceptively simple...
... but works surprisingly well!
- Works in *P1* symmetry
 - Space group used to locate origin
- Implemented in SUPERFLIP

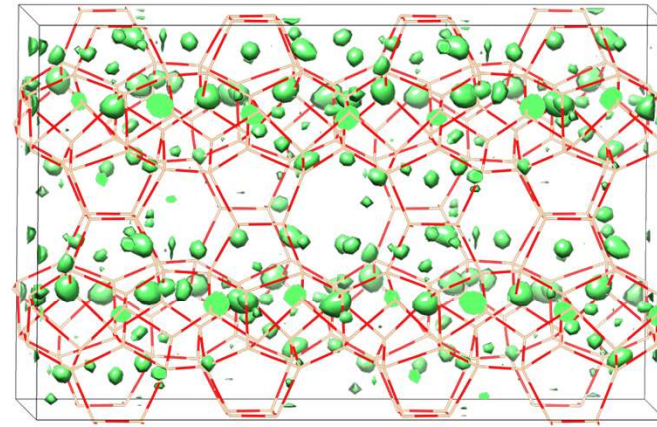


Oszlányi & Sütő, Acta Cryst. A, **2004**
Palatinus & Chapuis, J. of Appl. Cryst., **2007**

SUPERFLIP SSZ-45 with combined data

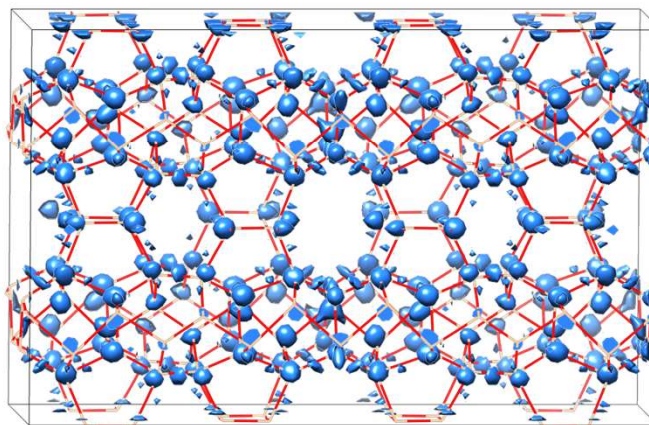
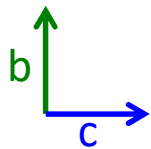


RED



XRPD

No solution possible from RED or XRPD data alone.

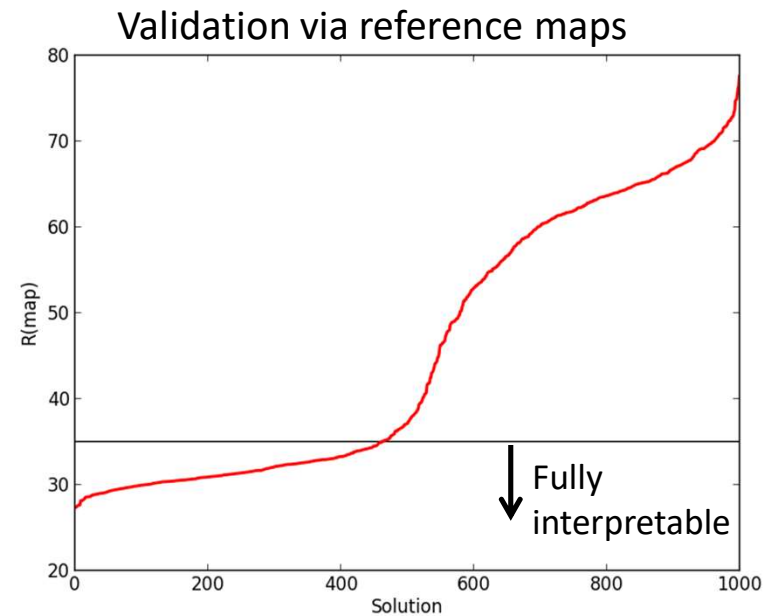
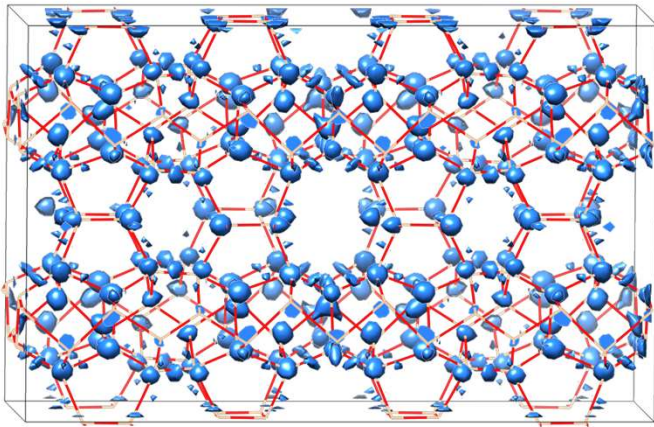


Combined

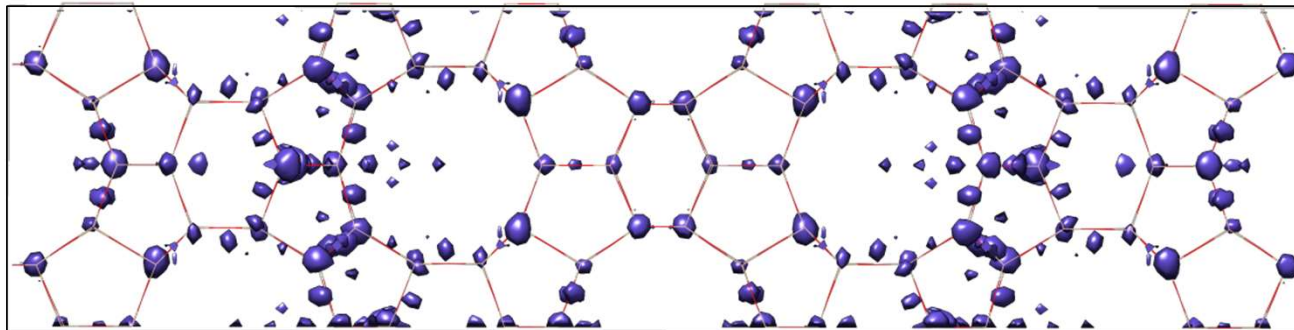
95% of framework atoms can be identified from density map!

SUPERFLIP SSZ-45 with combined data

- Structure solution directly from RED or XRPD data not possible
- 95% of Si and O atoms can be resolved
- Correct solution is generated in about 50% of trials



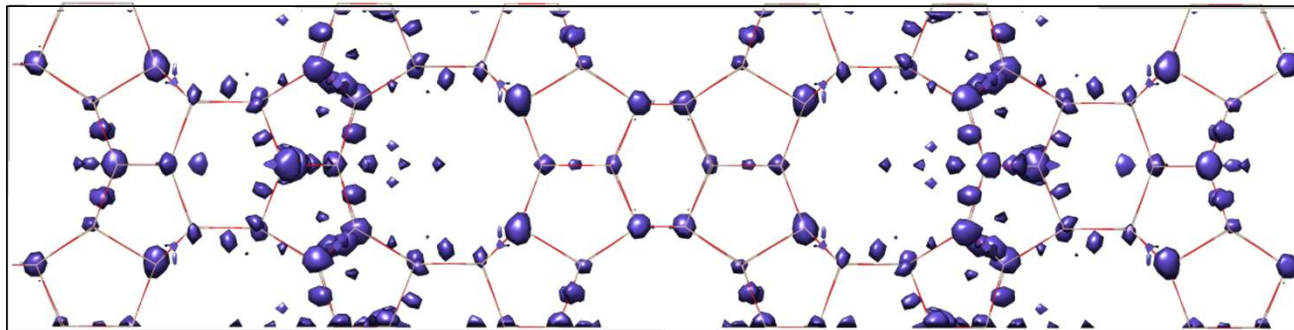
SUPERFLIP IM-5 with combined data



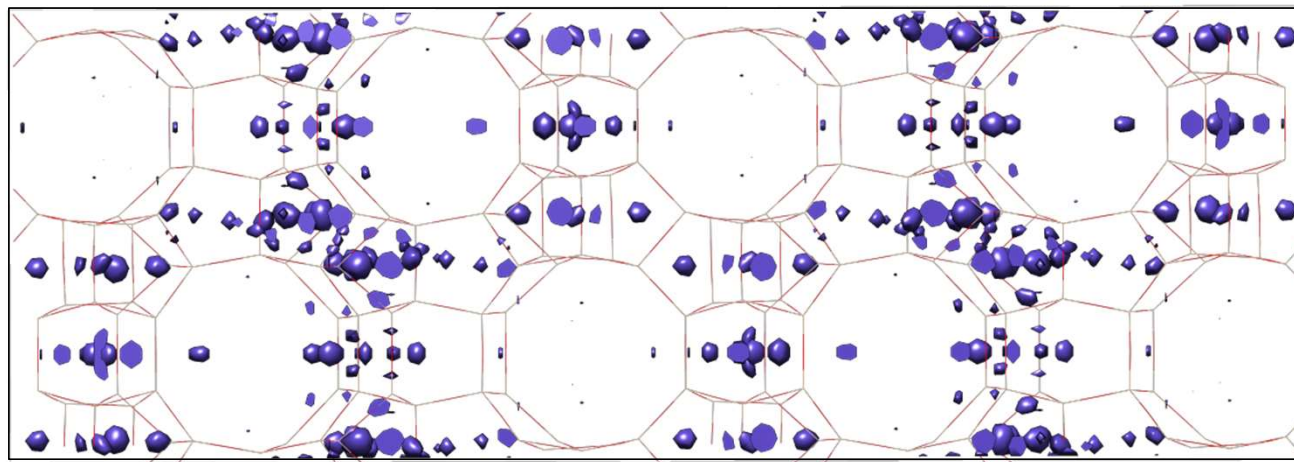
[0 0 1]

Looks pretty good along c!

SUPERFLIP IM-5 with combined data



[0 0 1]

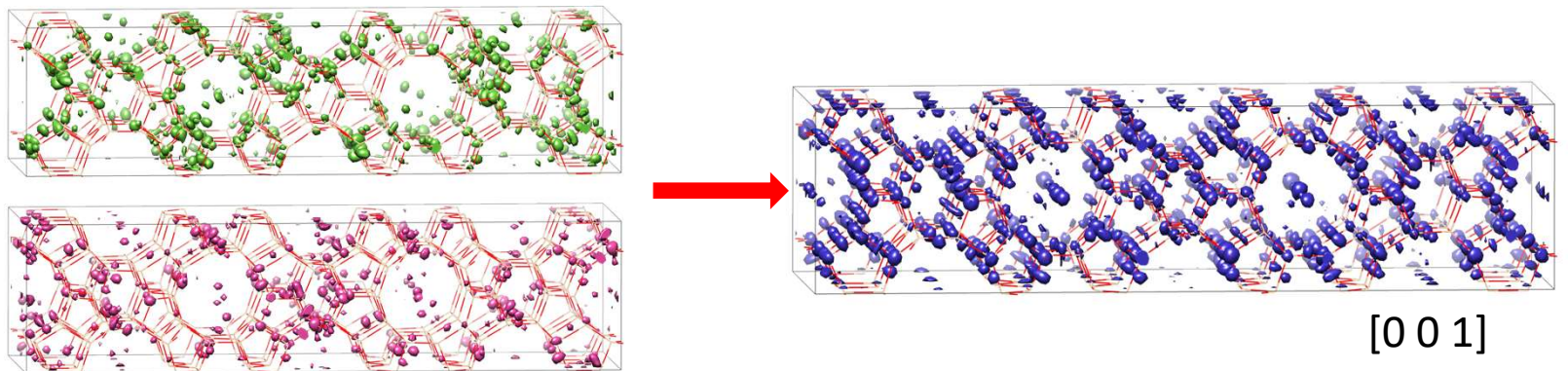


[1 0 0]

SUPERFLIP IM-5 with combined data

- Origin definition is problematic
 - Reliable procedure for finding origin under investigation
- 50-80% of all atoms can be identified from a single map (C1 symmetry)
 - Nearly all maps give partial solutions

Merging several good C1 maps aligned to reference maps:



Conclusions

- ED data is very well suited for use with FOCUS
 - FOCUS can compensate for low completeness/inaccurate reflections
 - Complicated structures (IM-5, ITQ-43) can be solved 'easily'
- Combined data set is more suited for structure solution
 - FOCUS finds more solutions faster
 - SUPERFLIP allows full solution where either XRPD or ED fail

Download FOCUS: www.iza-structure.org/

More details:

Smeets, S., McCusker, L. B., Baerlocher, C. B., Mugnaioli, E. & Kolb, U.

Using FOCUS to solve zeolite structures from three-dimensional electron diffraction data

J. Appl. Cryst., **2013**, 46, 1017-1023

Full pattern repartitioning

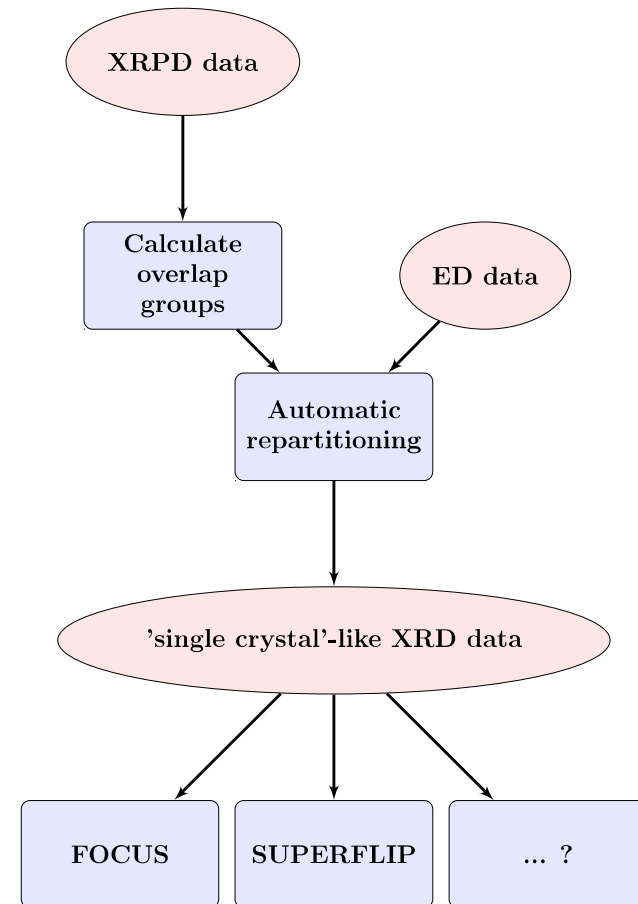
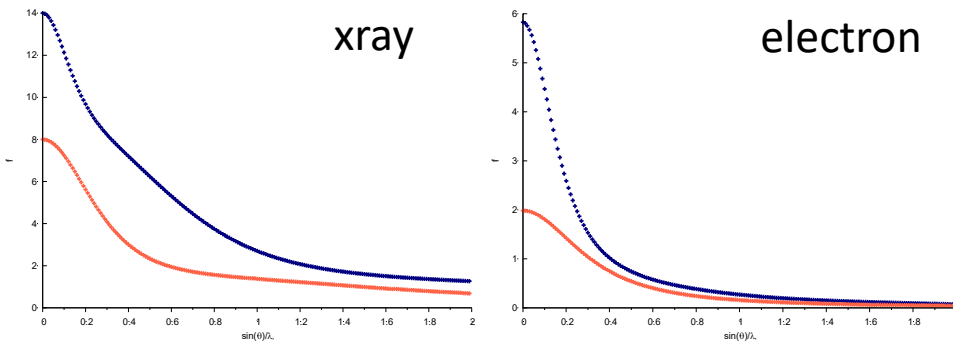
- Determine overlap groups:

$$2\theta_2 - 2\theta_1 < \frac{of}{2}(FWHM_1 + FWHM_2)$$

- Repartitioning:

$$|F^{x,new}|^2 = |F^{el}|^2 \frac{\sum_{\Gamma_k} m |F^x|^2}{\sum_{\Gamma_k} m |F^{el}|^2}$$

- Scattering factors **Si/O**



Overview of solutions

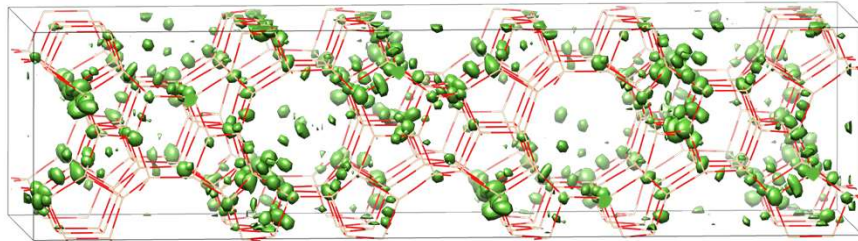
Sample	Natrolite	ZSM-5	ITQ-43	IM-5	SSZ-45	SSZ-45
Data	ADT	ADT	ADT	ADT	RED	XRPD
Space group	<i>Fdd2</i>	<i>Pnma</i>	<i>Cmmm</i>	<i>Cmcm</i>	<i>Fmmm</i>	<i>Fmmm</i>
a (Å)	18.293	20.100	26.411	14.209	13.6	13.7129
b (Å)	18.640	19.924	41.399	57.237	21.7	22.1253
c (Å)	6.586	13.424	12.839	19.994	35.03	35.1924
T-atoms	3	12	11	24	10	10
Refs. Used	200	200	200	200	200	200
Min. d-spacing (Å)	1.00	1.14	1.19	1.16	1.05	1.18
% coverage	100	81	98	95	53	100
Trials	2000	2815	16156	100000	8000	155147
Solutions	3938	311	1898	595	351	238
Correct	2340	300	1791	587	142	108
% correct	59	96	94	99	40	45
CPU time (hr)	0.10	6	4	24	1.33	20
Rate (sec/sol)	0.15	72	8	147	34	667

FOCUS with combined data

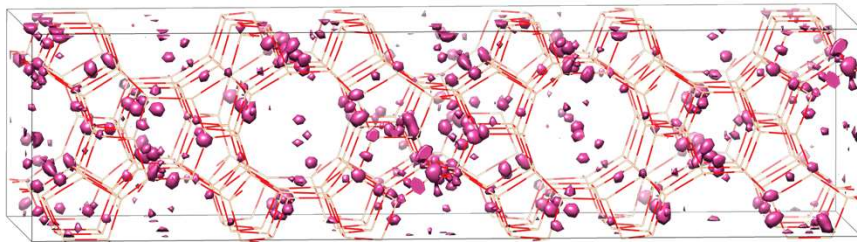
- Using combined data shows significant improvements
- Setting the right overlap groups is crucial for success
 - of=0.3 is traditionally used and often sufficient
 - of=1.2 proved most successful for IM5, found by trying a range from 0.1 – 3.0
 - Not all overlap factors benefited structure solution

	Data	Overlap factor	Overlap %	Trials	Solutions	Correct	% correct	CPU time (hr)	Rate (sec/sol)
ZSM5	XRPD	0.3	72	4009	436	429	98	3.5	29
	ADT	–	–	2815	311	300	96	6.0	72
	combined	0.3	72	8000	5670	5656	100	3.4	2
SSZ45	XRPD	0.3	80	155147	238	108	45	20.0	667
	RED	–	–	8000	351	142	40	1.3	34
	combined	0.3	80	50000	3429	2579	75	5.6	8
IM5	ADT	–	–	100000	595	587	99	24.0	147
	combined	1.2	97	50000	598	597	100	6.5	63

SUPERFLIP IM-5 with combined data



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