

FEZA, Sofia, BG  
06-07-2017

# Characterization of zeolites using powder diffraction: framework structures, heteroatoms, OSDAs

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Stockholm University, Sweden



SWISS NATIONAL SCIENCE FOUNDATION

**ETH** zürich

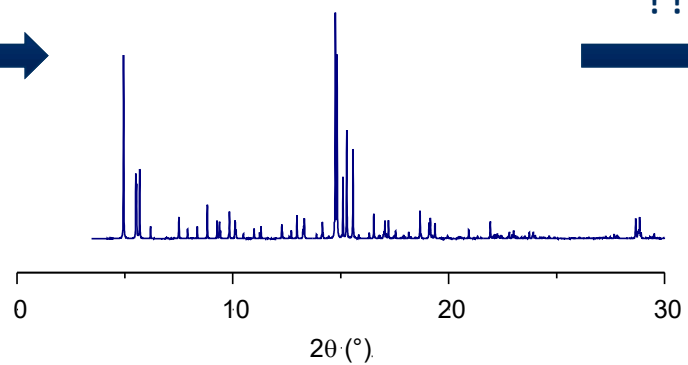


Stockholm  
University

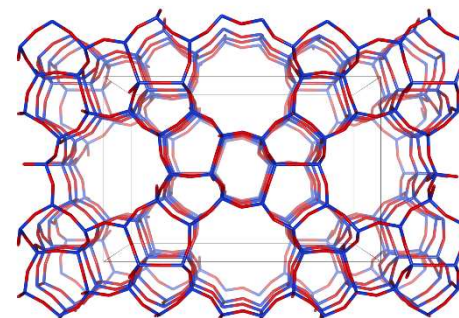
# X-ray Powder Diffraction



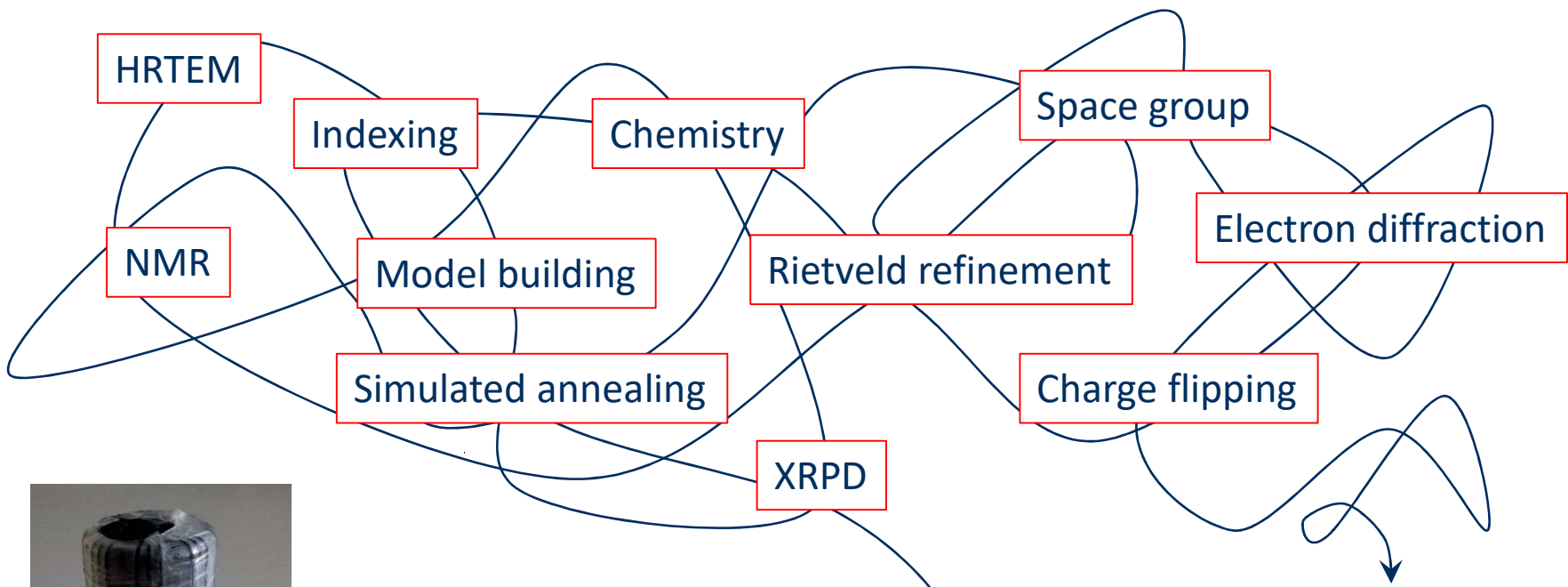
Prepare



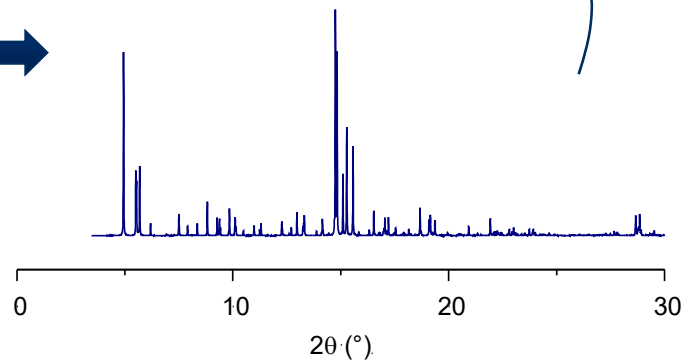
Measure



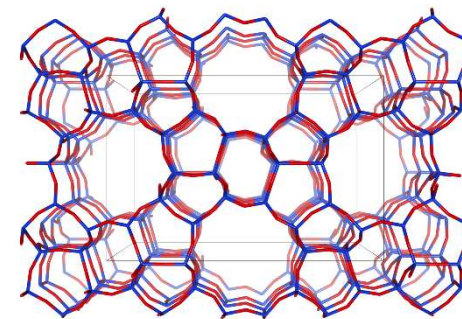
Characterize



Sample



Characterize



Structure

# Outline

- Structure of SSZ-70
  - Layered, disordered zeolite related to **MWW**
  - Promising catalytic properties
- Structure of SSZ-87
  - Medium-pore zeolite
  - Characteristics of a large pore one
- Serial electron diffraction
  - New method for data collection

# SSZ-70

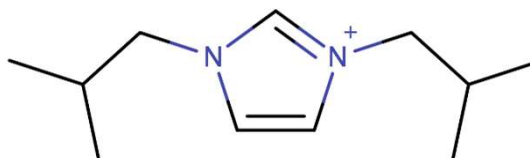
S. Smeets, Z. J. Berkson, D. Xie, S. I. Zones, W. Wan, X. Zou,  
M.-F. Hsieh, B. F. Chmelka, L. B. McCusker, C. Baerlocher,  
*In manuscript.*

# Zeolite SSZ-70

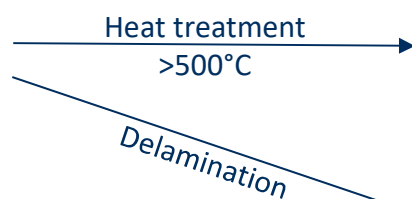
Stacey Zones and Alan Burton,  
US Patent 7,108,843 B2, 2006

*Molecular sieve SSZ-70 composition of matter and synthesis thereof*

Structure-directing agent

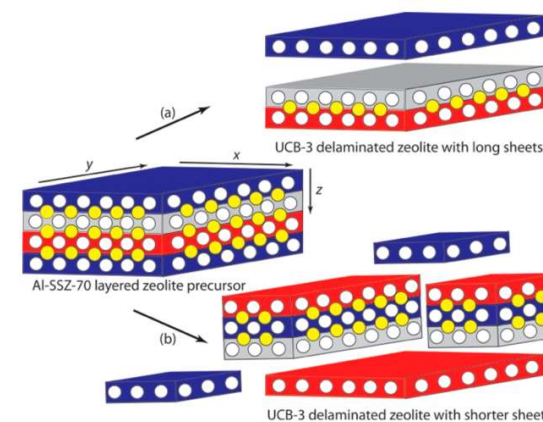


Pure silicate  
Borosilicate  
Aluminosilicate

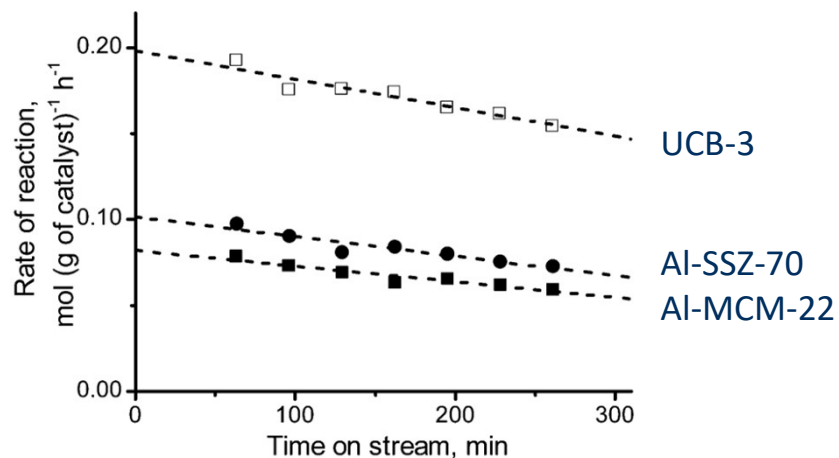


Calcined  
SSZ-70

UCB-3 (A)  
UCB-4 (B)

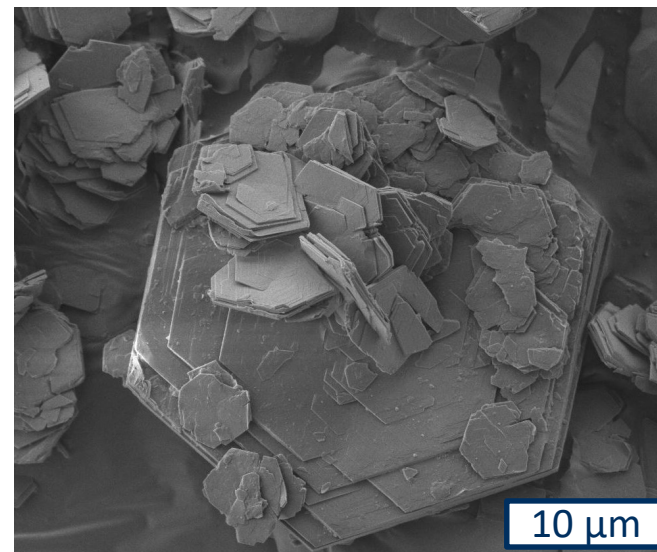
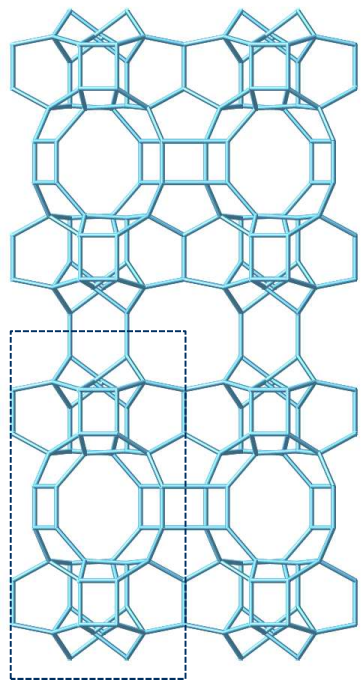


Catalysis: aromatic alkylation



# As-made Si-SSZ-70

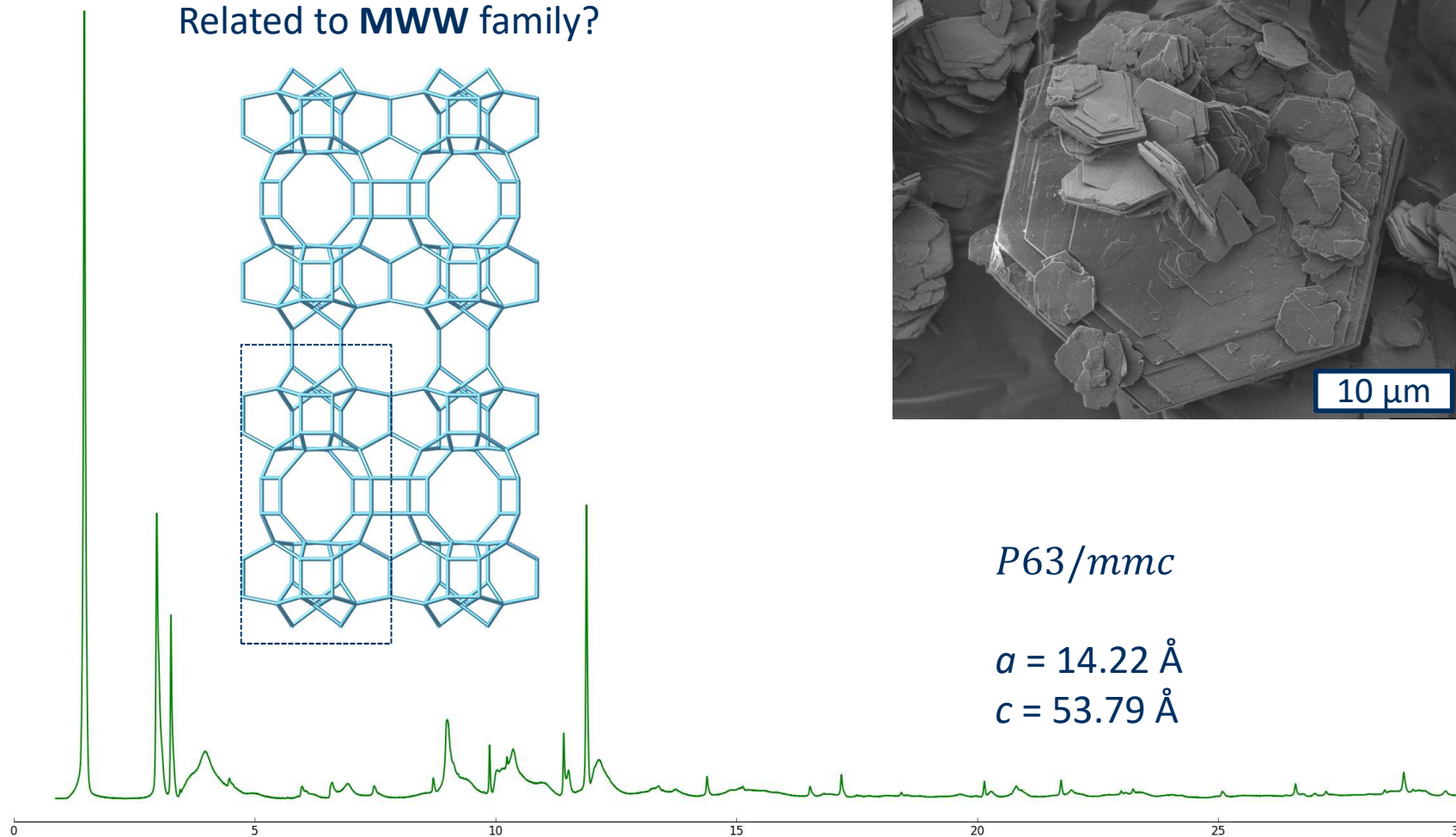
Related to **MWW** family?



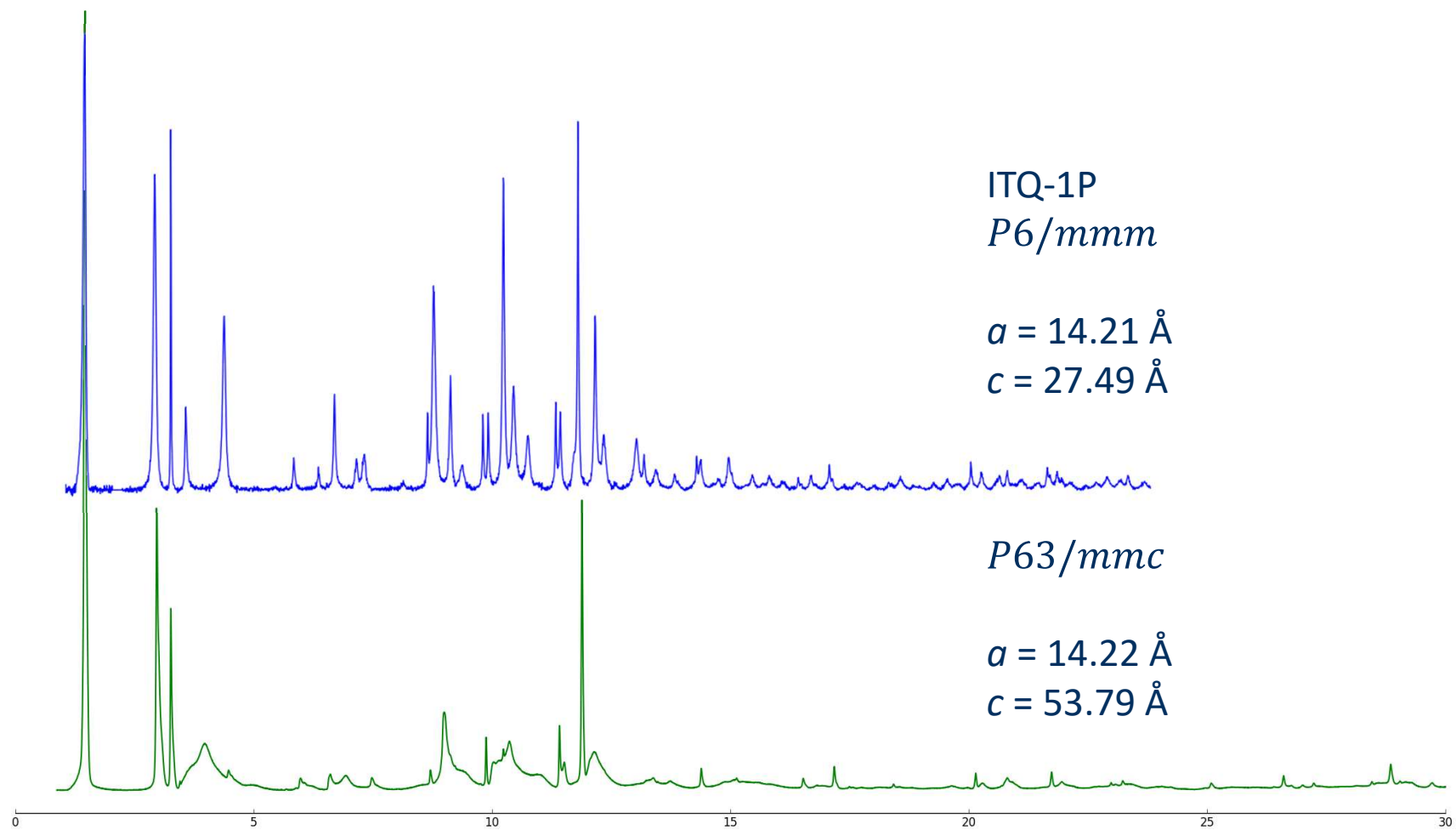
$P63/mmc$

$a = 14.22 \text{ \AA}$

$c = 53.79 \text{ \AA}$

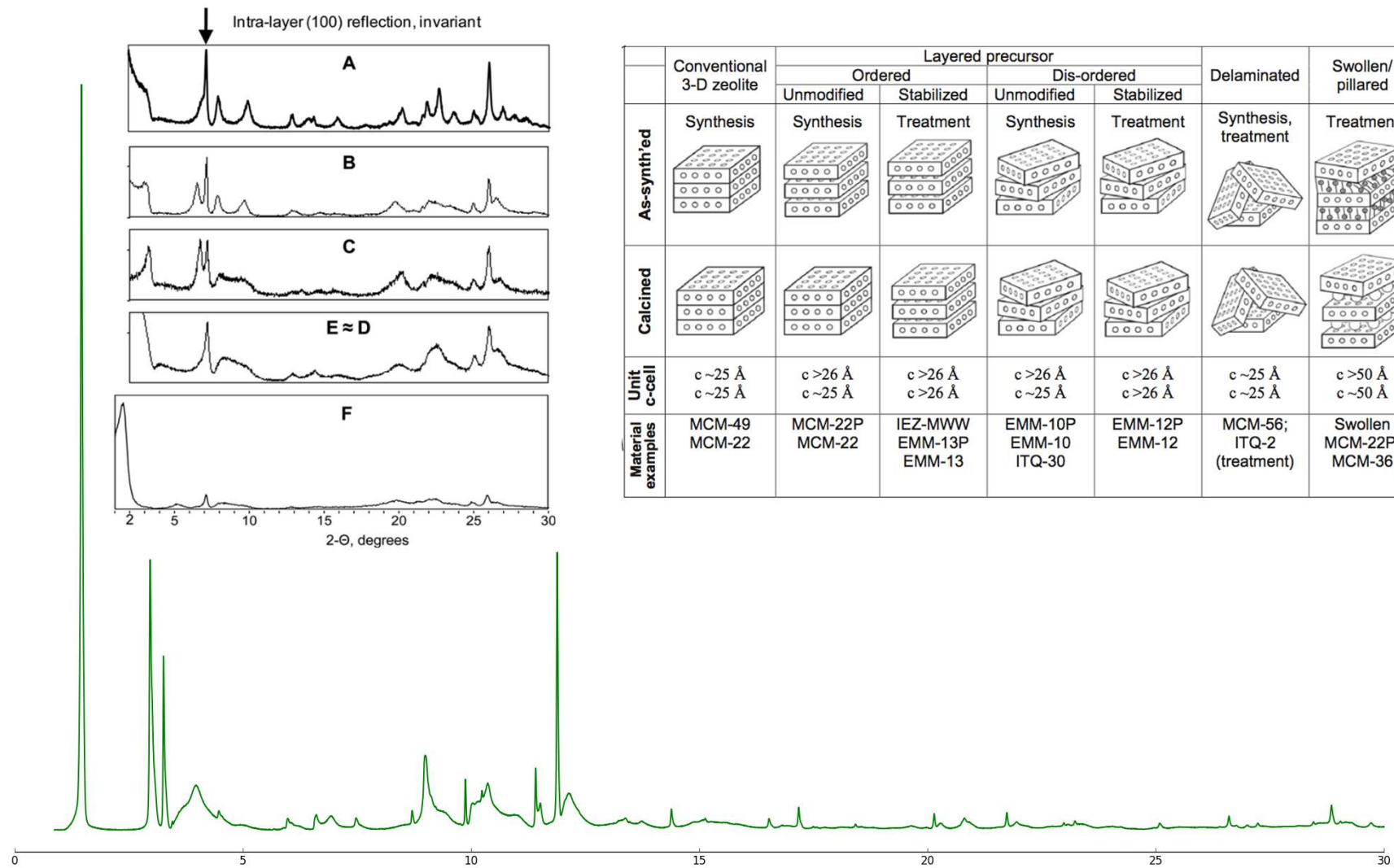


# As-made Si-SSZ-70



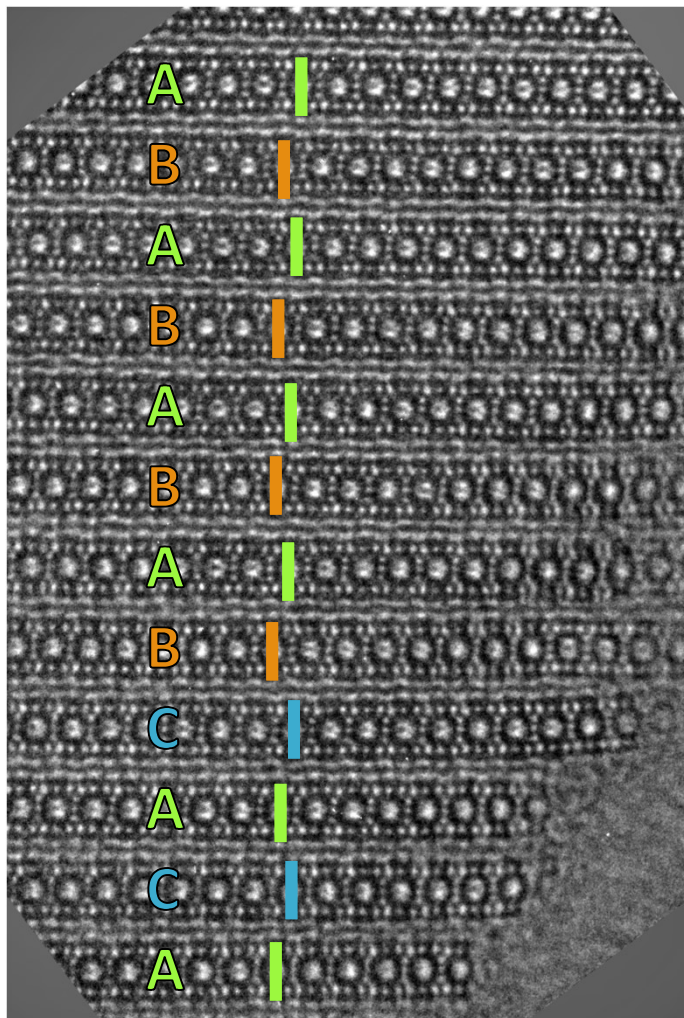


# As-made Si-SSZ-70

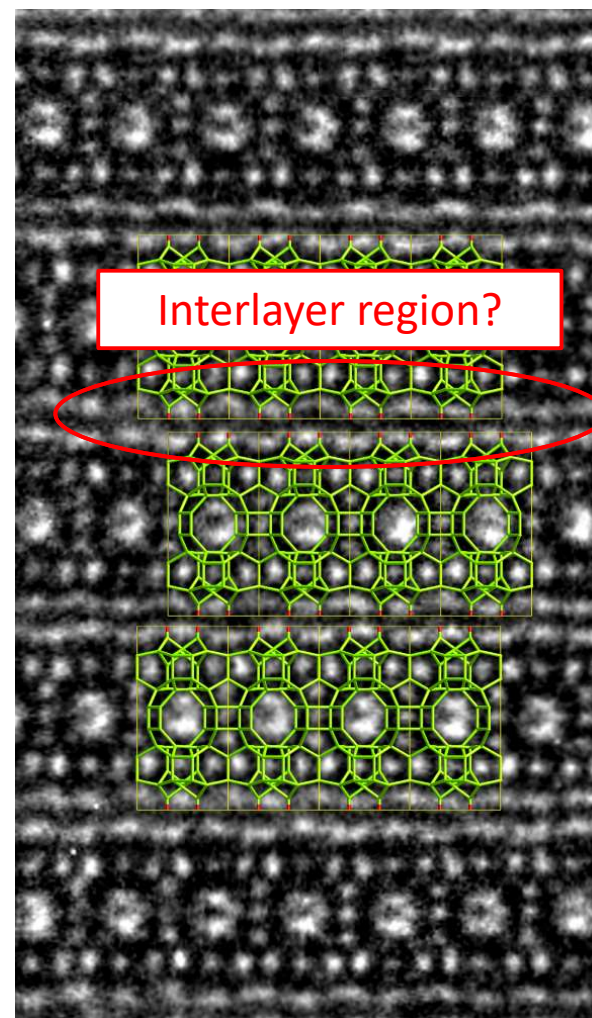


# HRTEM

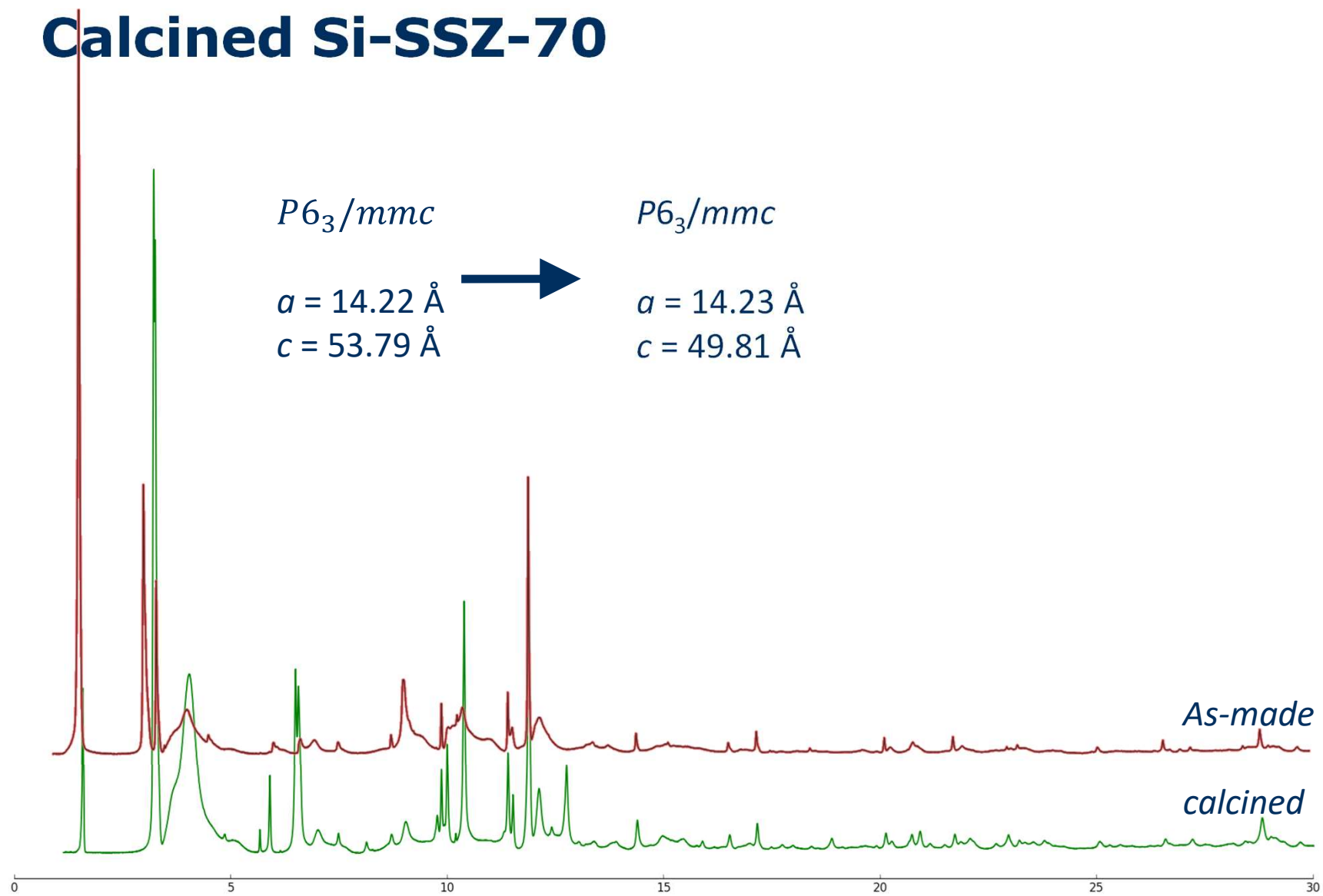
Stacking disorder along [001]



MWW-layers

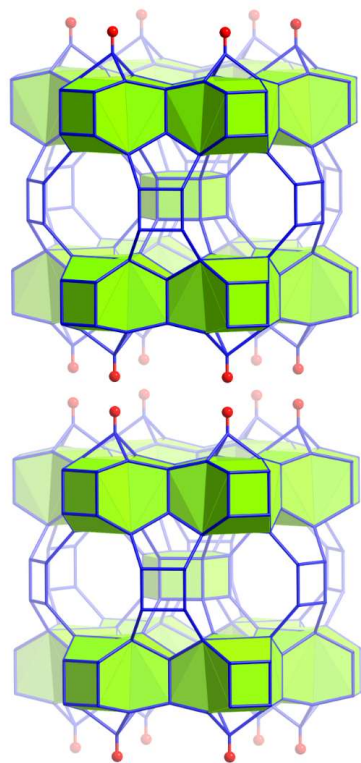


# Calcined Si-SSZ-70



# ITQ-1 (MWW)

$P6/mmm$   
 $a = 14.21 \text{ \AA}$   
 $c = 27.49 \text{ \AA}$

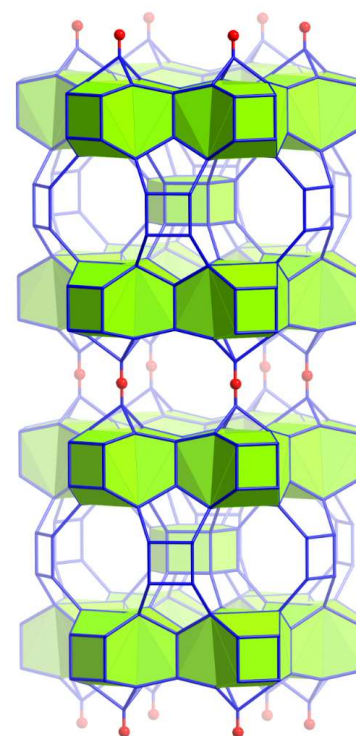


ITQ-1P

Njo, *PhD thesis, TU Delft* (1998)

Condenses  
upon calcination  
→

$P6/mmm$   
 $a = 14.21 \text{ \AA}$   
 $c = 24.94 \text{ \AA}$



MWW  
layer

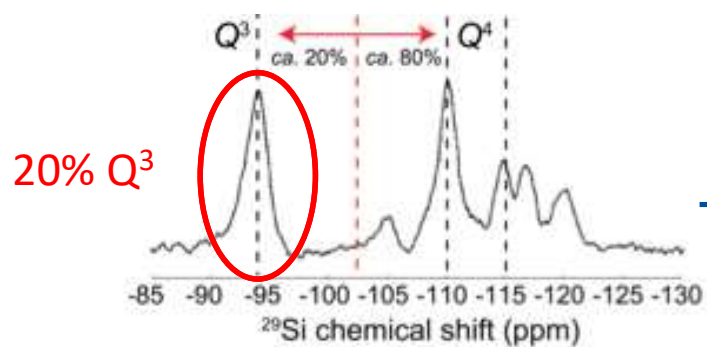
ITQ-1

Camblor *et al.*, *J. Phys. Chem. B*, **102**, 44 (1998)

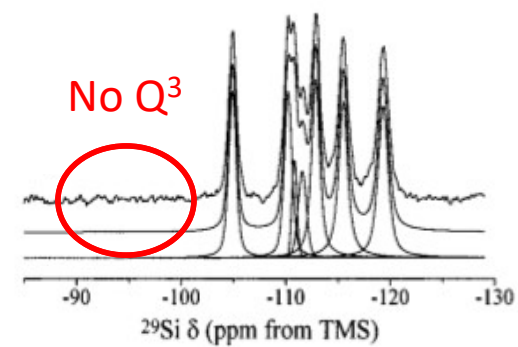
# Solid-state $^{29}\text{Si}$ MAS NMR

As-made

Calcined



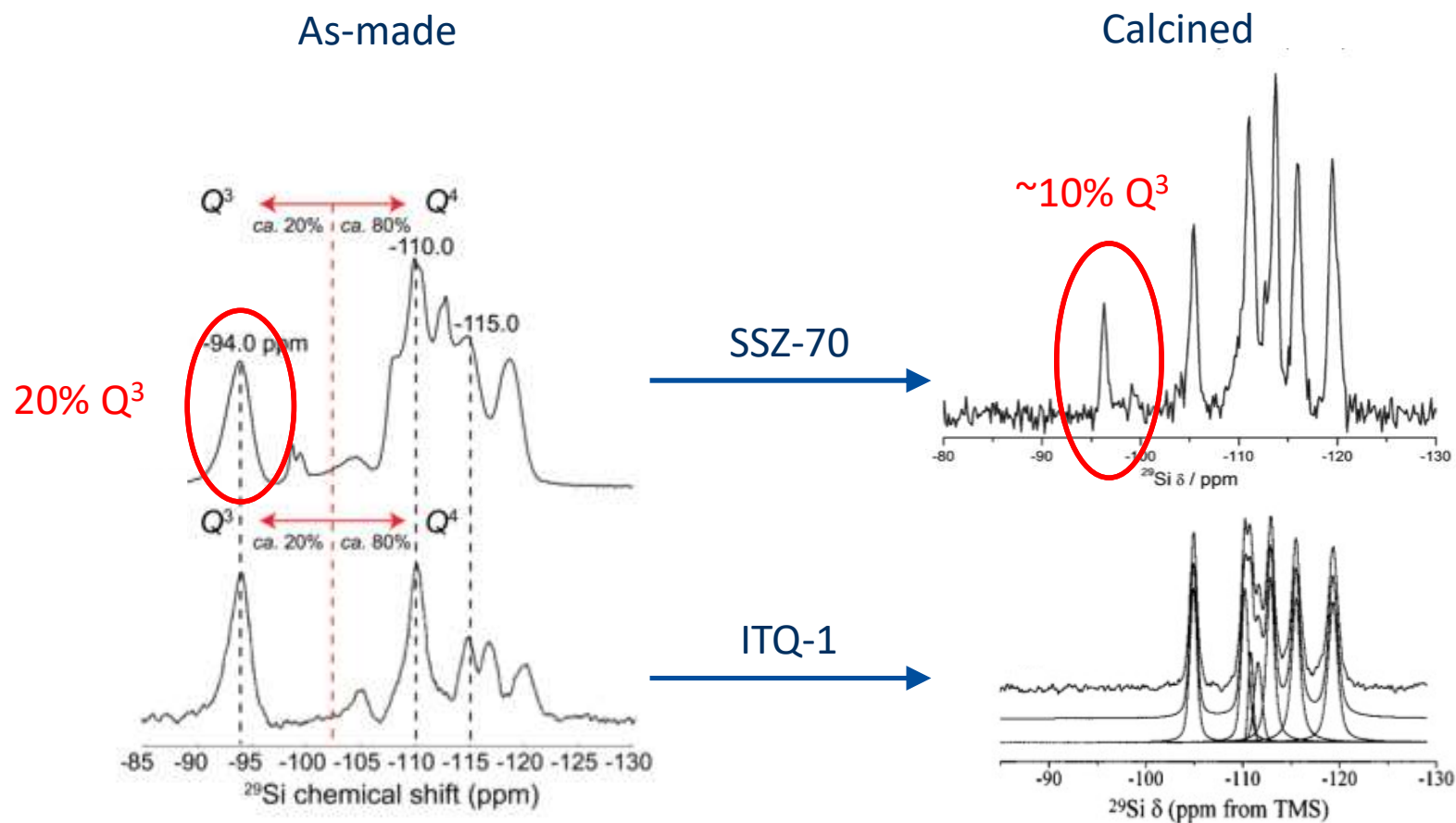
ITQ-1



Hsieh, Aronson and Chmelka (2014)

Archer *et al.*, *Micropor. Mesopor. Mat.*, **130**, 255 (2010)  
Cambor *et al.*, *J. Phys. Chem. B*, **102**, 44 (1998)

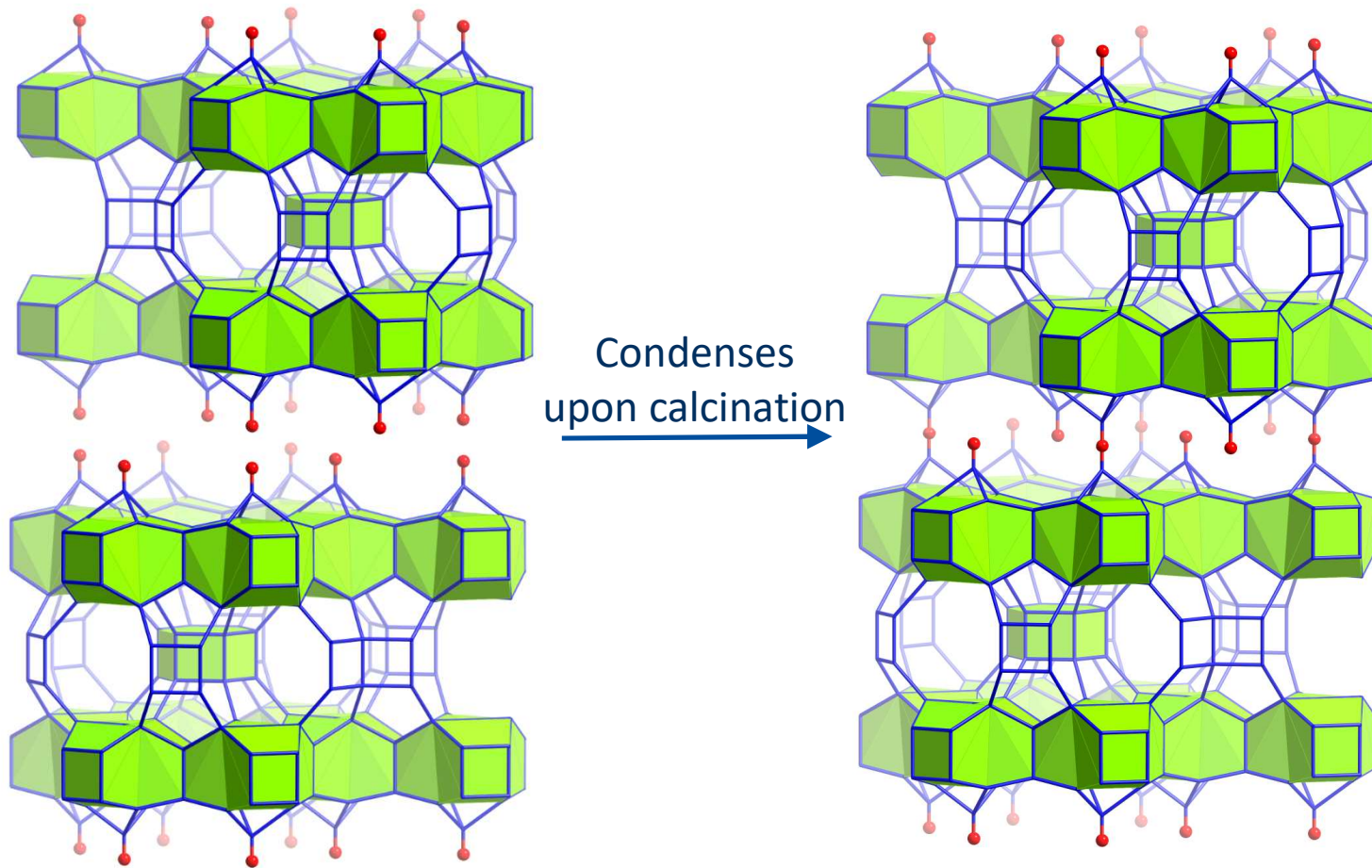
# Solid-state $^{29}\text{Si}$ MAS NMR



Hsieh, Aronson and Chmelka (2014)

Archer *et al.*, *Micropor. Mesopor. Mat.*, **130**, 255 (2010)  
Cambor *et al.*, *J. Phys. Chem. B*, **102**, 44 (1998)

# Model for SSZ-70



As-made SSZ-70

Calcined SSZ-70

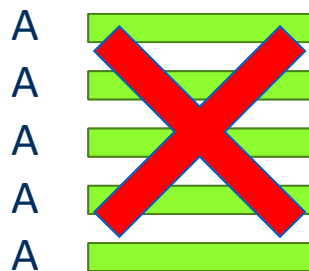
# Disorder model

Random arrangement of **MWW** layers  
Model with DiFFaX

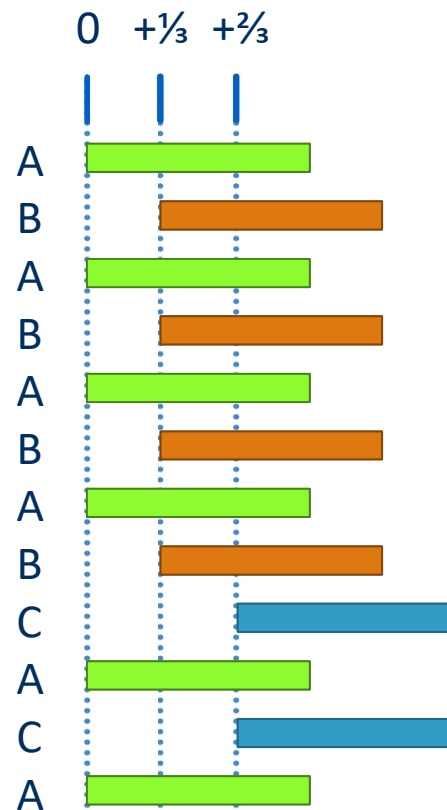
$$P(A \rightarrow A) = 0\%$$

$$P(A \rightarrow B) = 50\%$$

$$P(A \rightarrow C) = 50\%$$



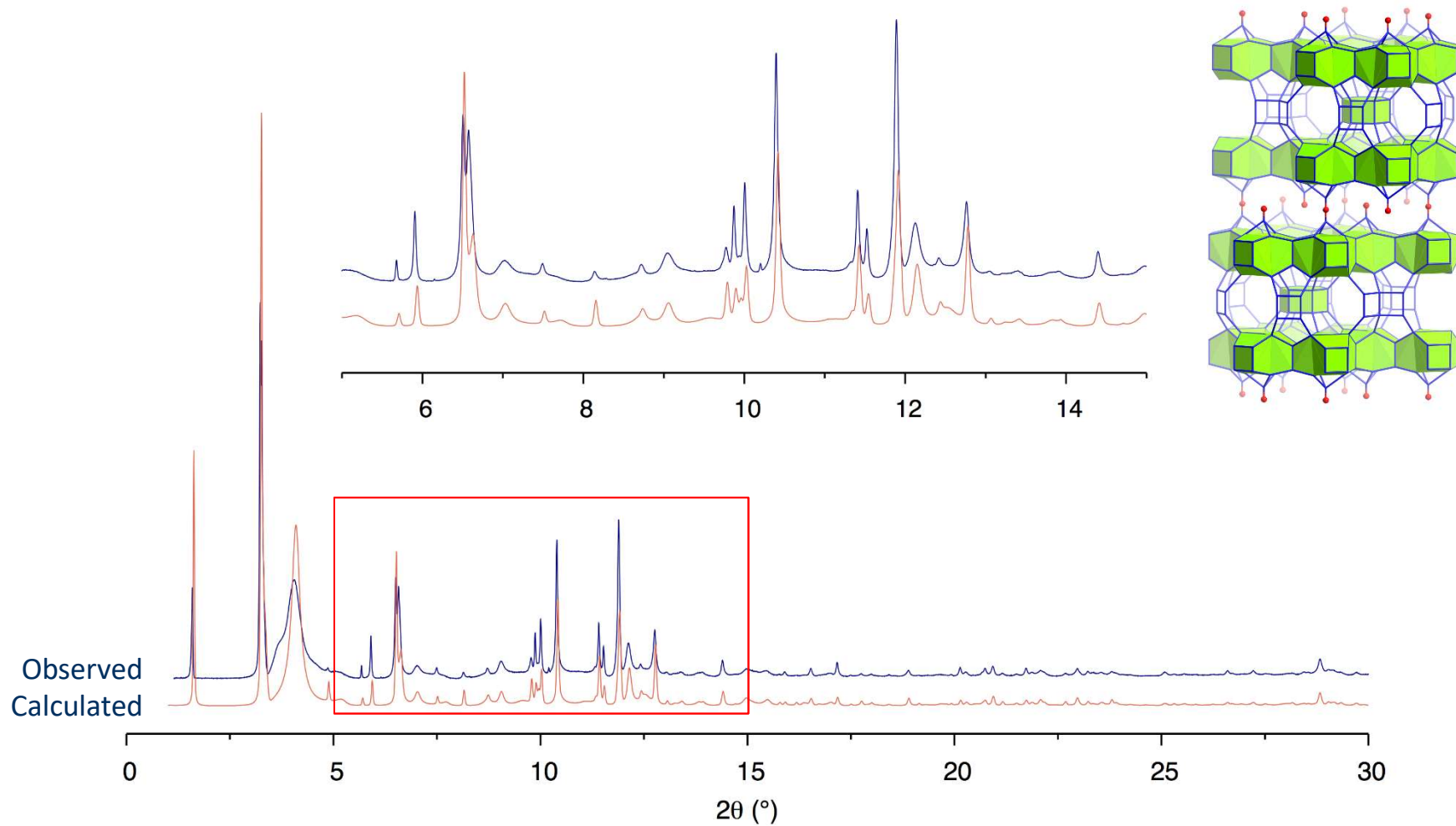
**ITQ-1**



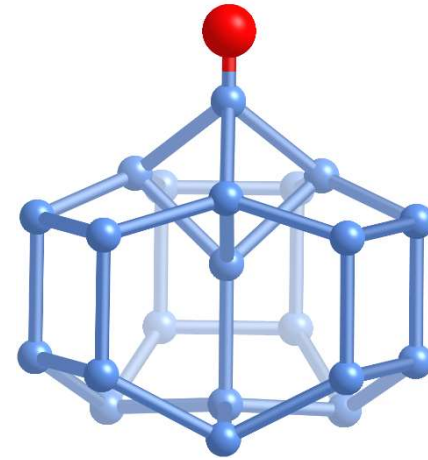
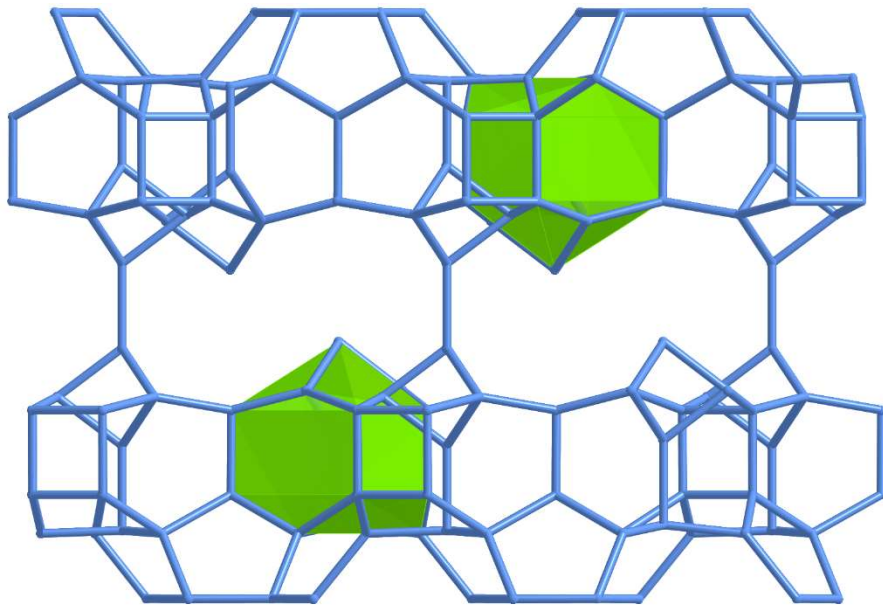
**SSZ-70**



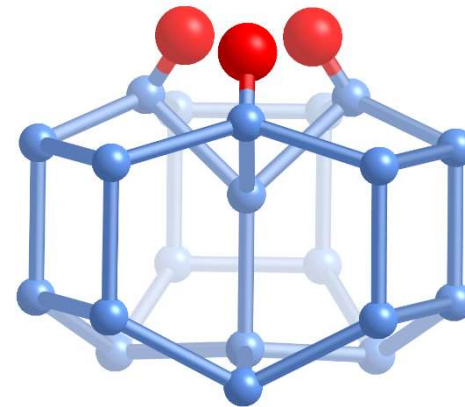
# Calcined SSZ-70



# Interlayer region

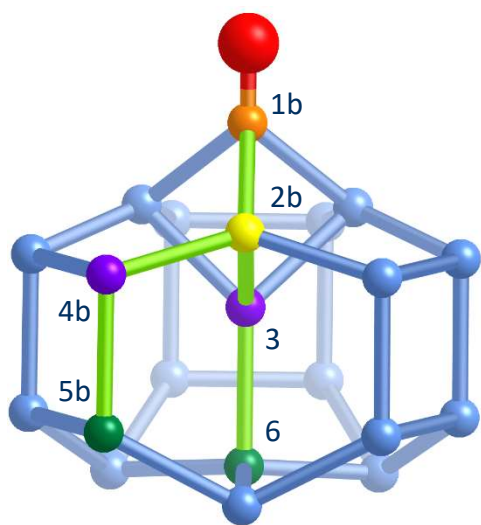


Model 1

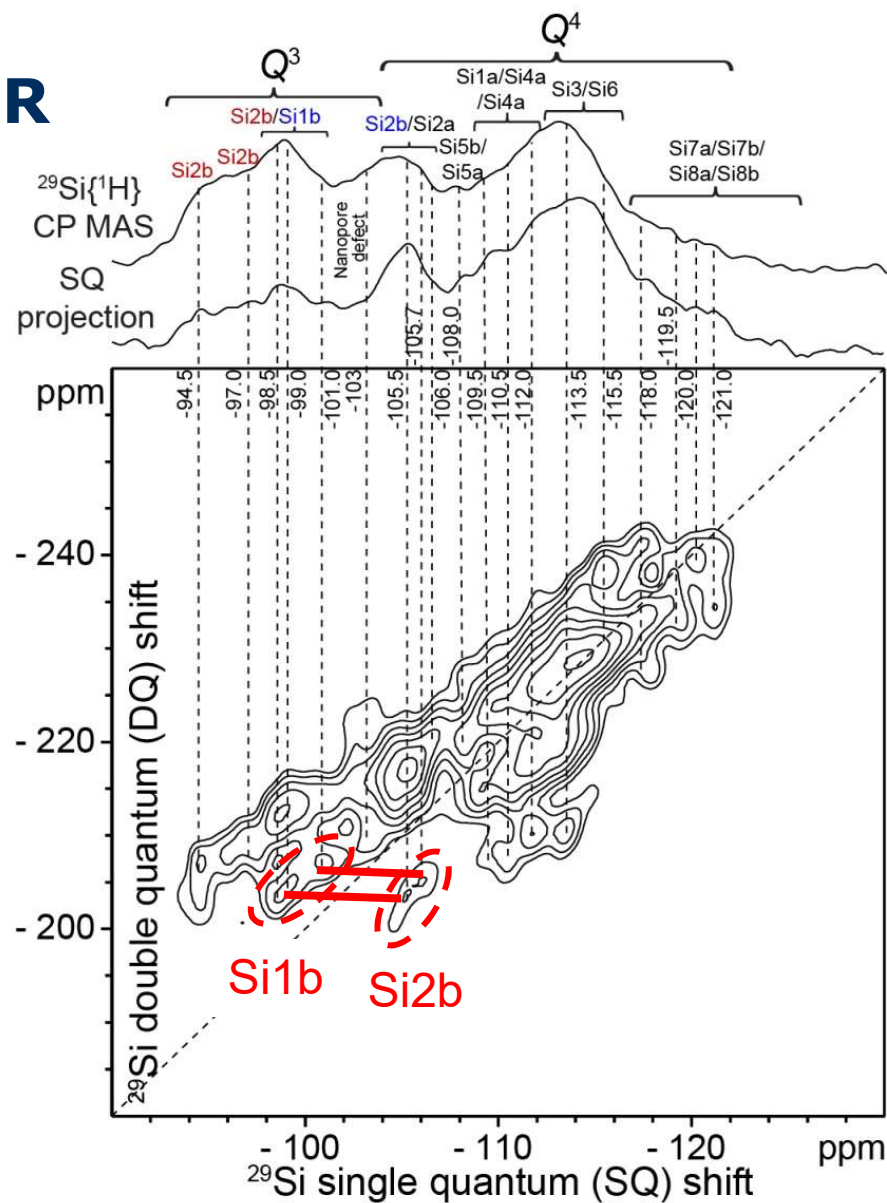


Model 2

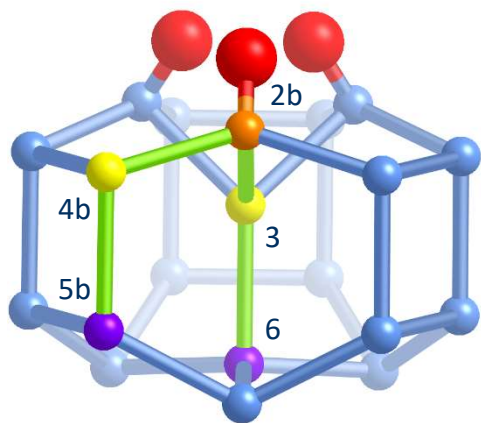
# 2D $J$ -mediated DNP-enhanced $^{29}\text{Si}\{^{29}\text{Si}\}$ NMR



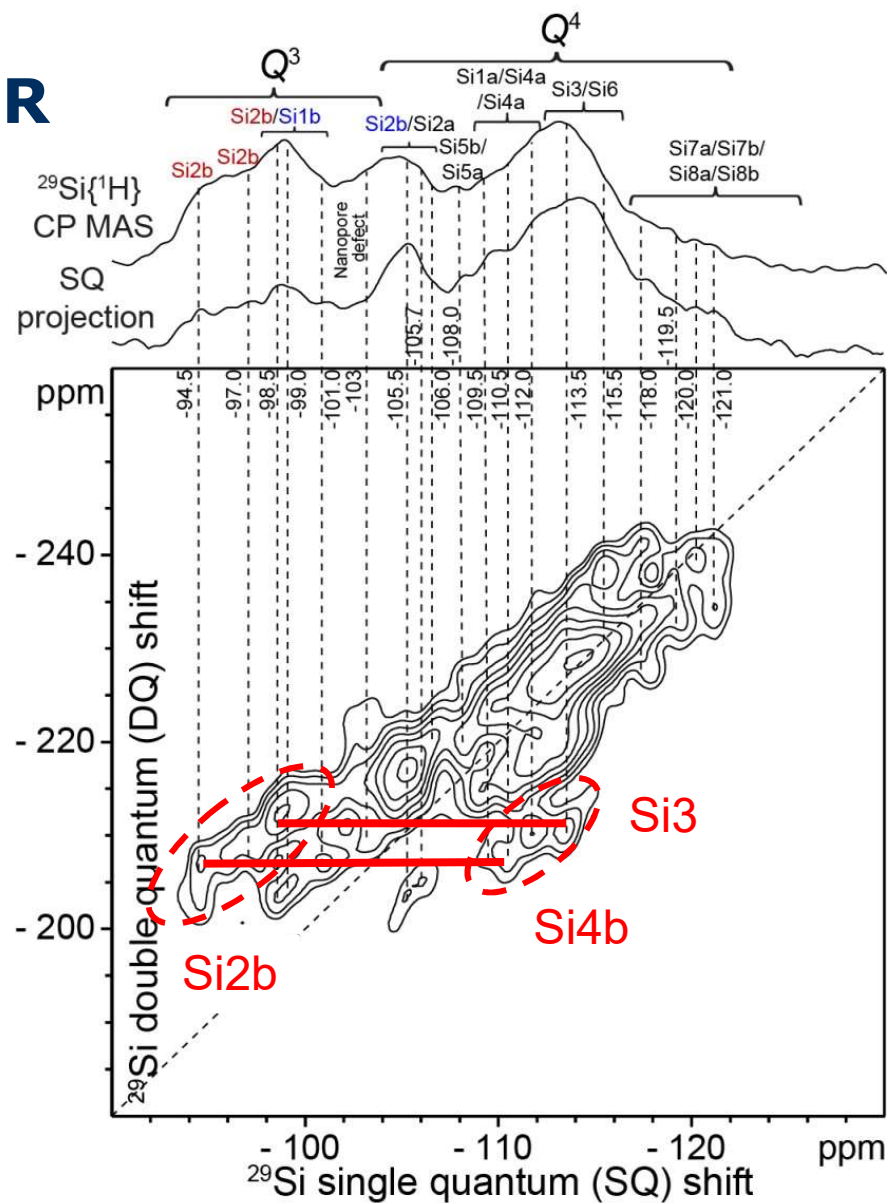
Model 1



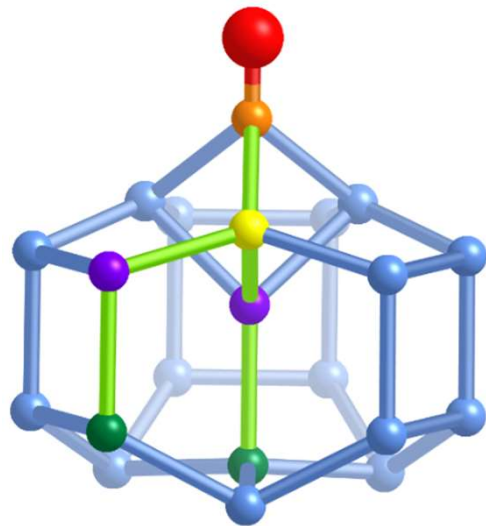
# 2D $J$ -mediated DNP-enhanced $^{29}\text{Si}\{^{29}\text{Si}\}$ NMR



Model 2

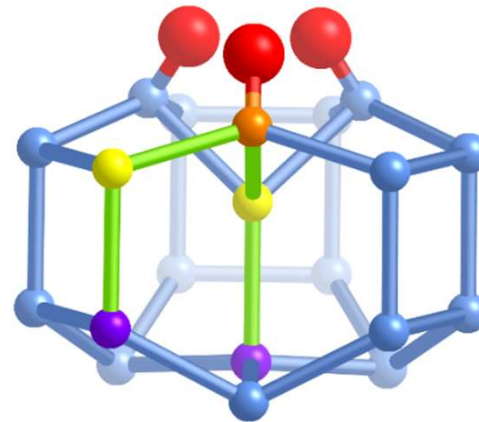


# Interlayer region



Model 1

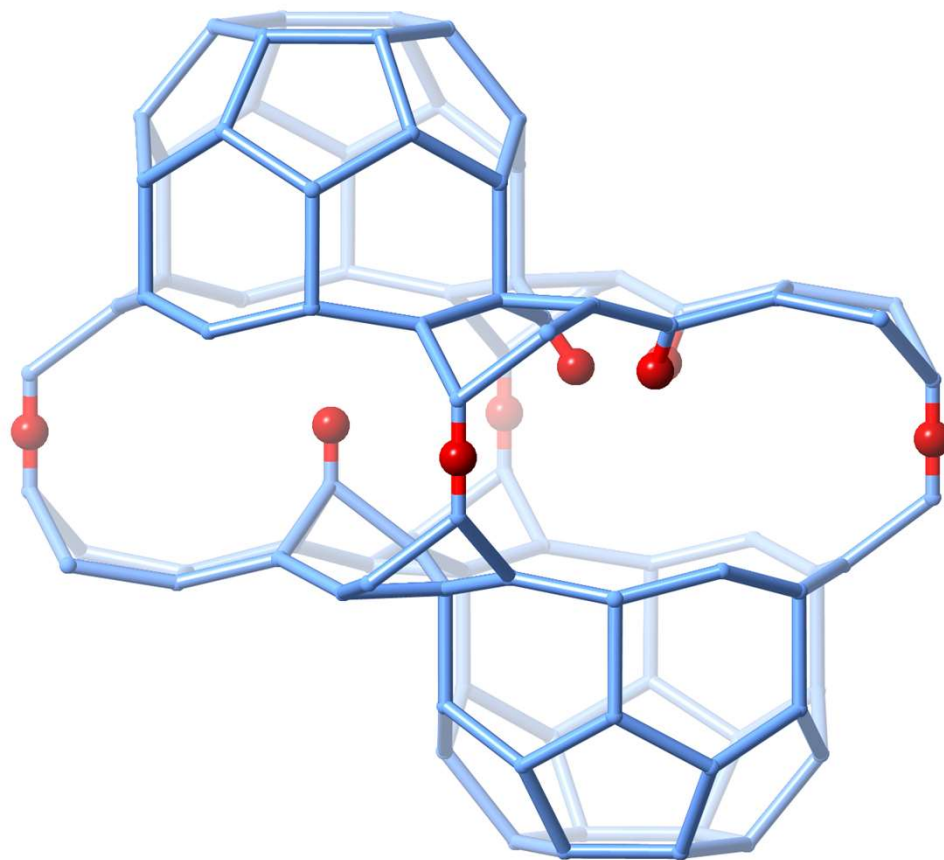
50%



Model 2

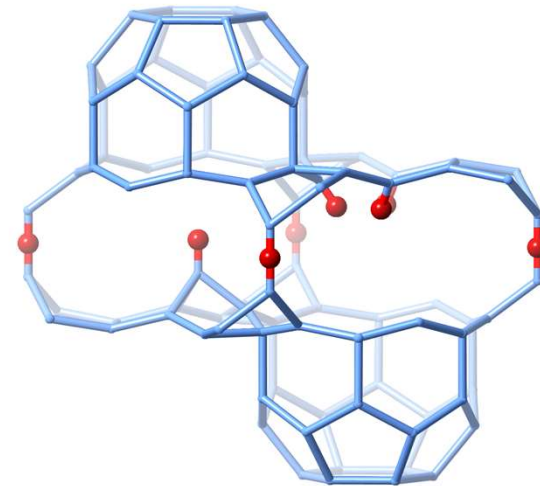
50%

## Structure of SSZ-70



# Summary

- Structure of SSZ-70 solved by combining methods
  - HRTEM → Disorder
  - XRPD → Average structure
  - NMR → Local structure
- New stacking arrangement of **MWW**-layers
- Open interlayer channel system
  - 14-ring pores (4.0 x 11.5 Å)



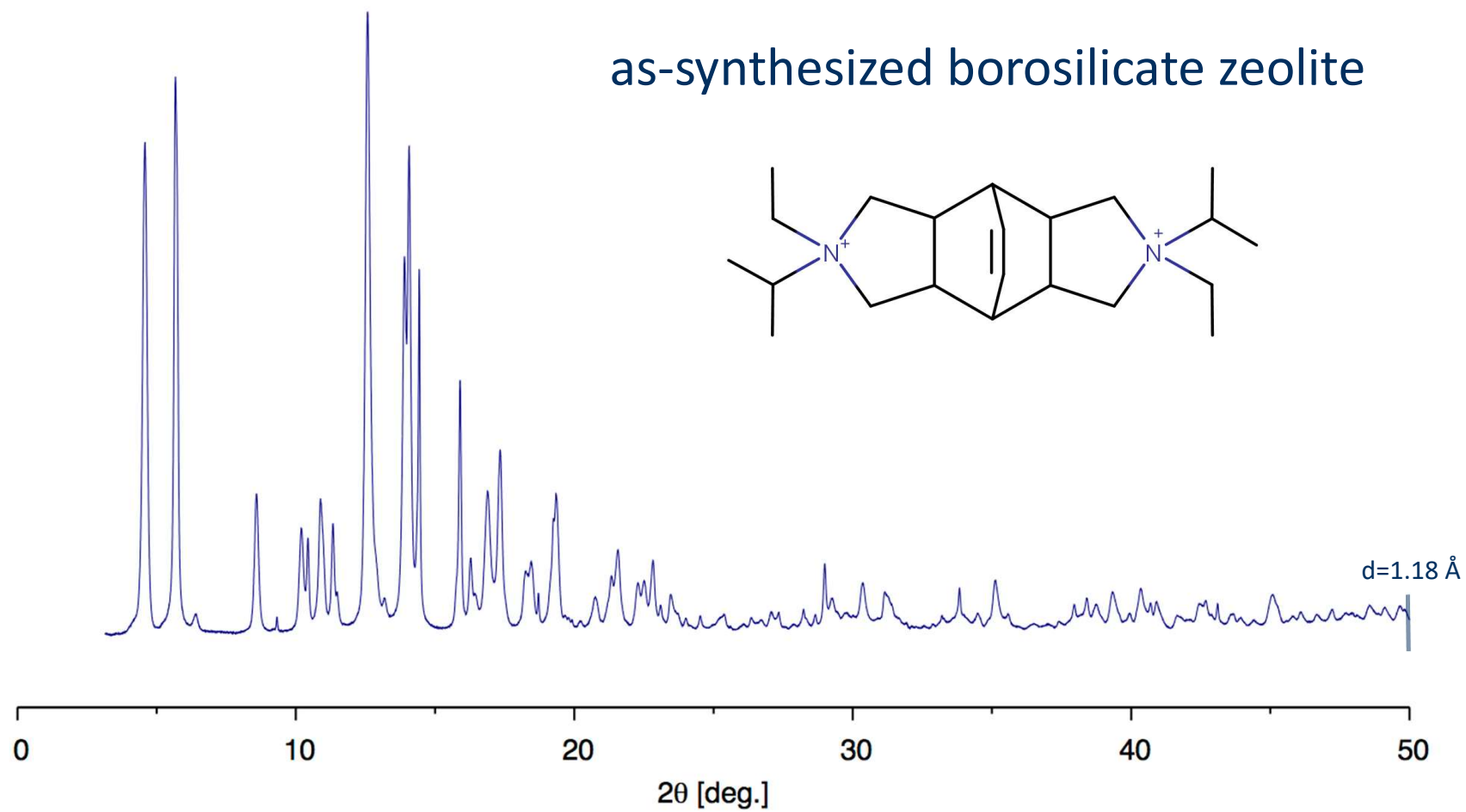
# SSZ-87

S. Smeets, L. B. McCusker, C. Baerlocher, D. Xie, C.-Y. Chen, S. I. Zones,  
*J. Am. Chem. Soc.* **137**, 2015-2020 (2015)

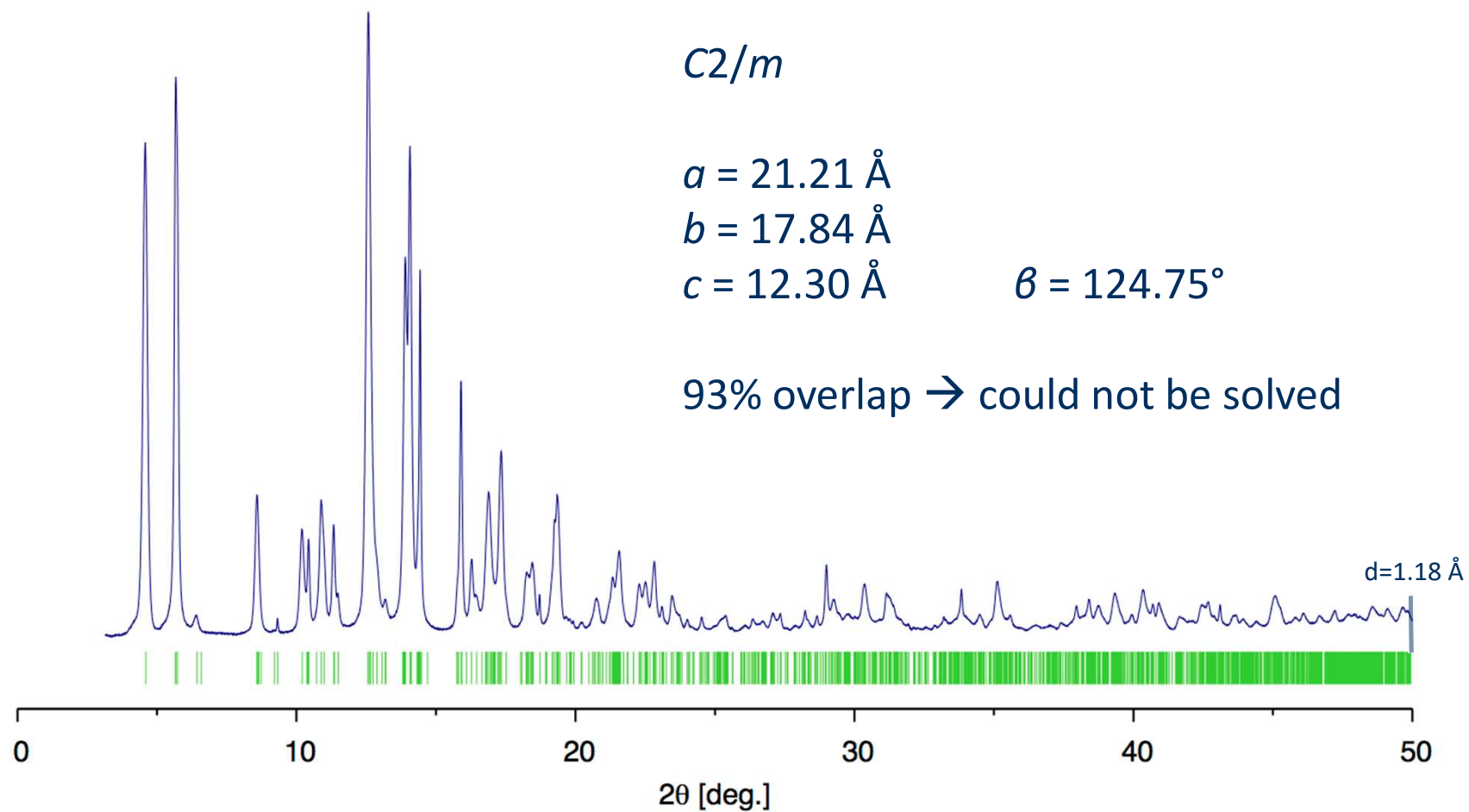


# SSZ-87

as-synthesized borosilicate zeolite

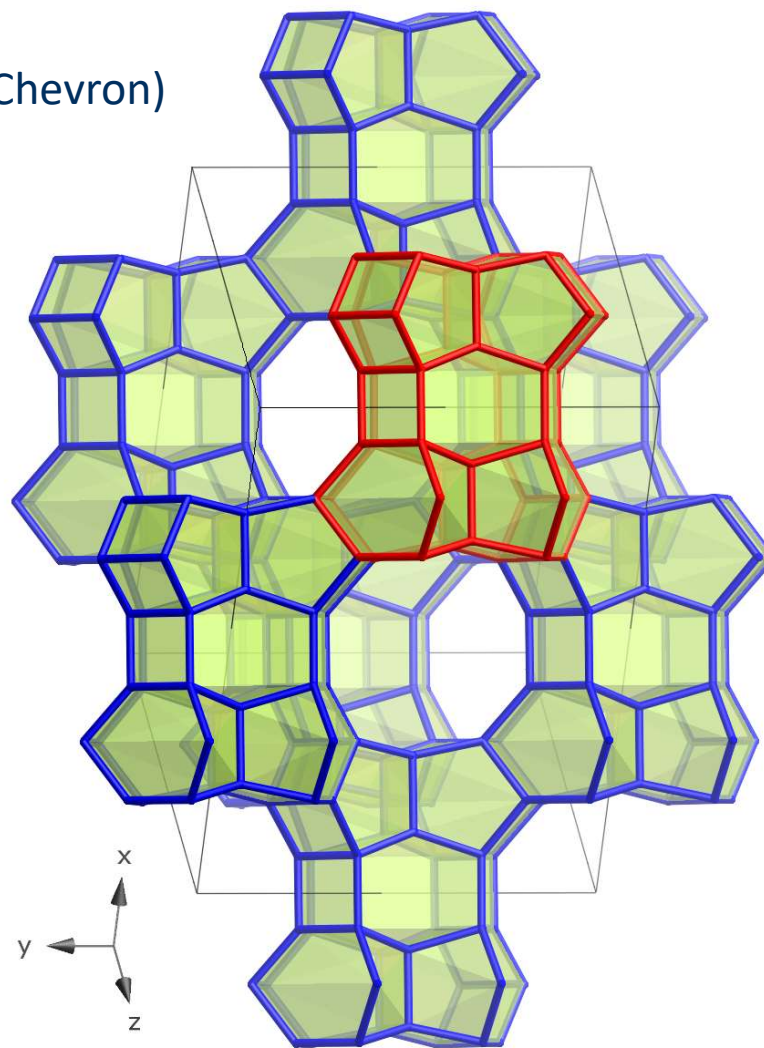
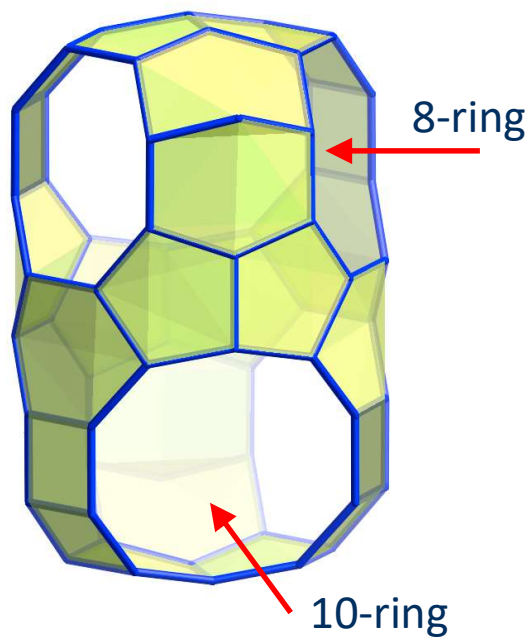


# Indexing of SSZ-87

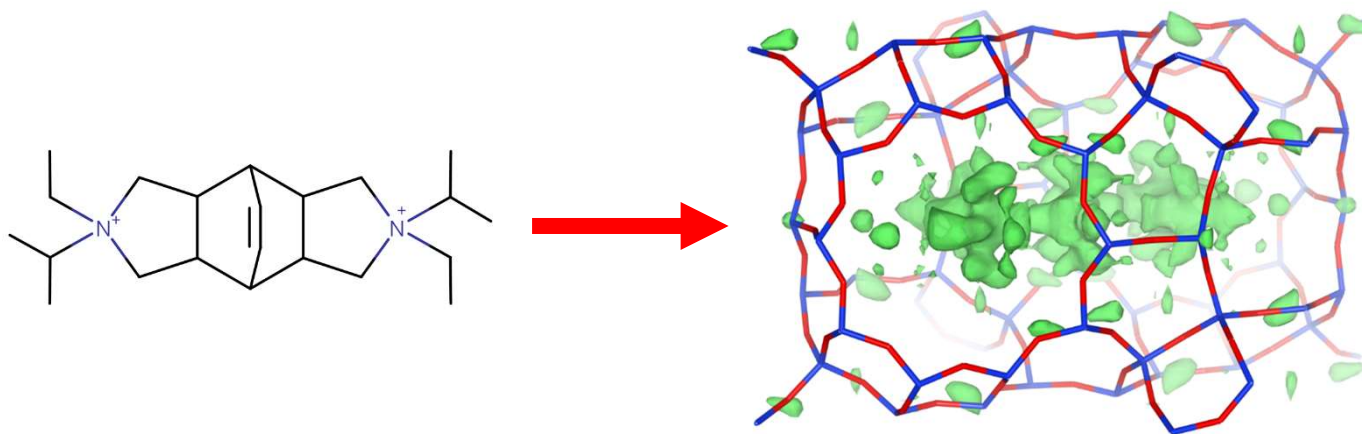


# Framework structure

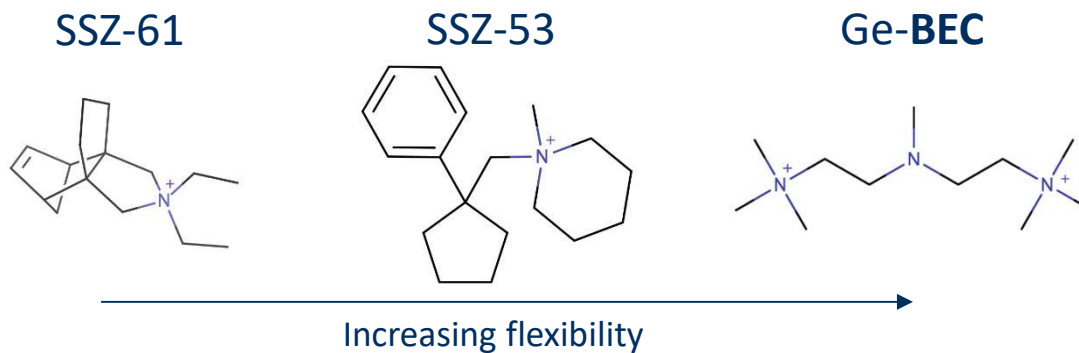
- Rotation electron diffraction data (Tom Rea, Chevron)
- Solved with FOCUS
- Same topology as ITQ-52 (**IFW**)
- Large cavity delimited by 14-ring
- Interconnected via 8/10-ring windows



# Locating the OSDA



Using simulated annealing:

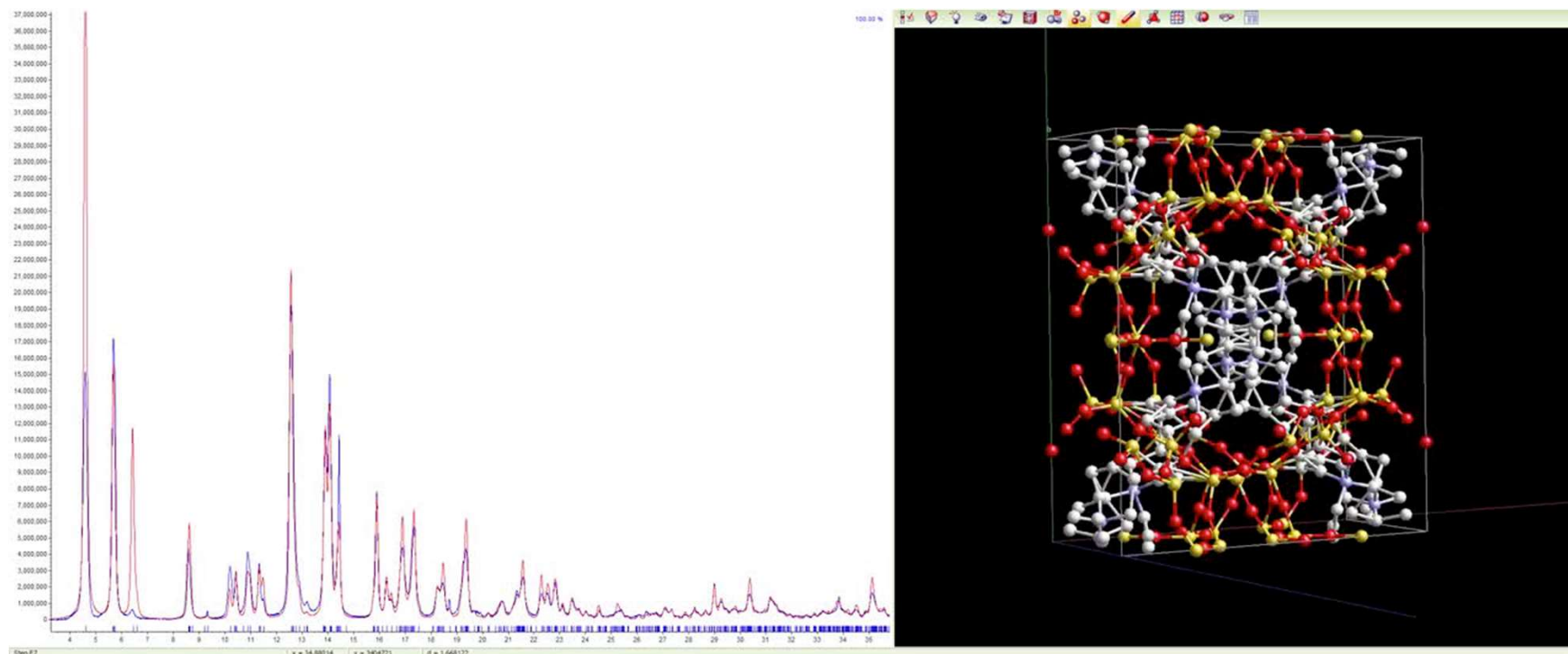


S. Smeets, L. B. McCusker, C. Baerlocher, S. Elomari, D. Xie, and S. I. Zones,  
*J. Am. Chem. Soc.* **138**, 7099-7106 (2016)



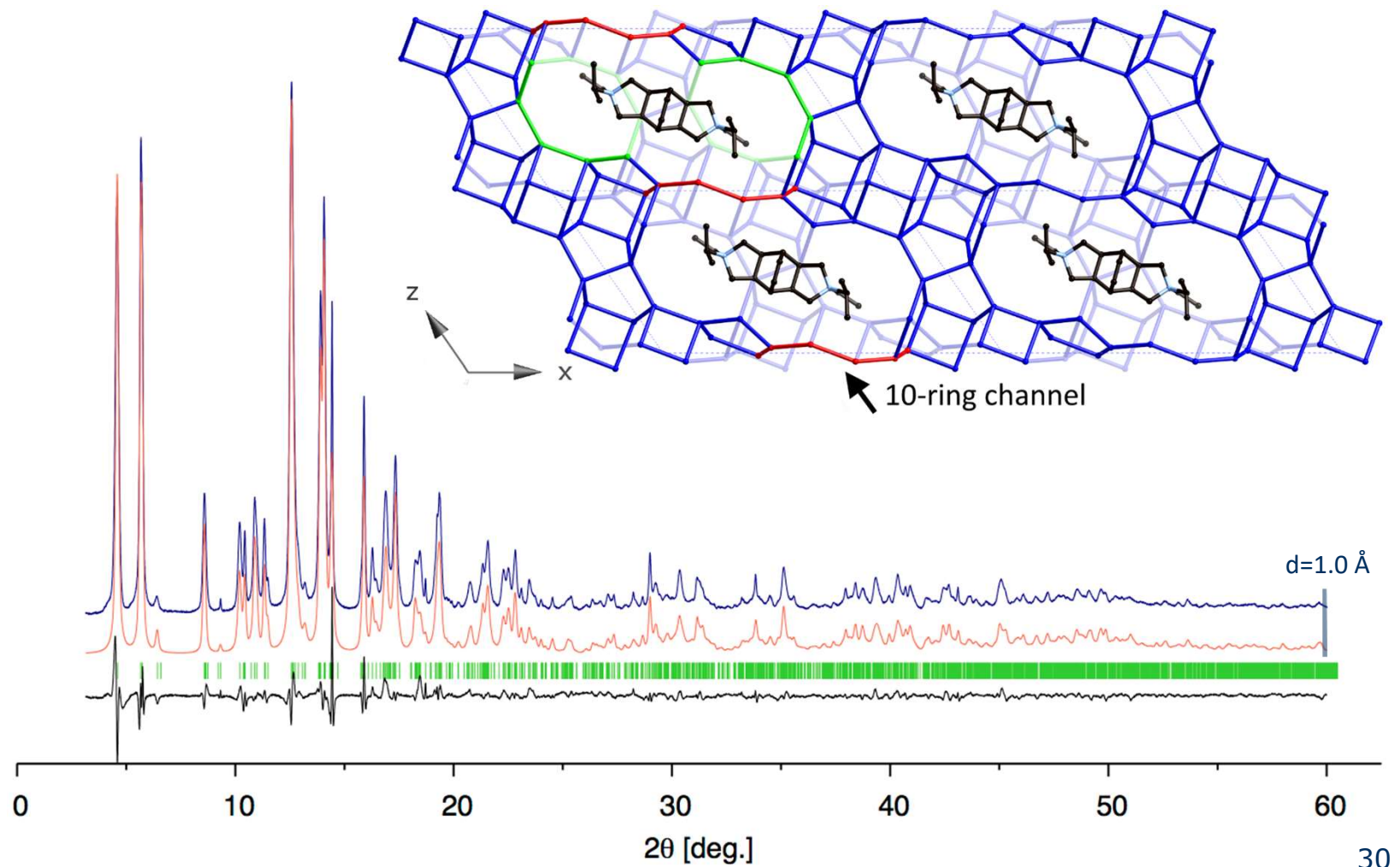
# Locating the OSDA

Using simulated annealing



S. Smeets, L. B. McCusker, C. Baerlocher, S. Elomari, D. Xie, and S. I. Zones,  
*J. Am. Chem. Soc.* **138**, 7099-7106 (2016)

# Refinement of as-synthesized SSZ-87



# Al insertion in borosilicates

Zeolite	Channel system	Final pH	Wt% Al
		After 96h, 95°C	
ZSM-11 ( <b>MEL</b> )	10-ring	3.00	0.01
SSZ-57 ( <b>*SFV</b> )	10(12)-ring	2.24	0.30
SSZ-33 ( <b>CON</b> )	12-ring	1.36	1.10
SSZ-87 ( <b>IFW</b> )	10-ring	1.44	0.95

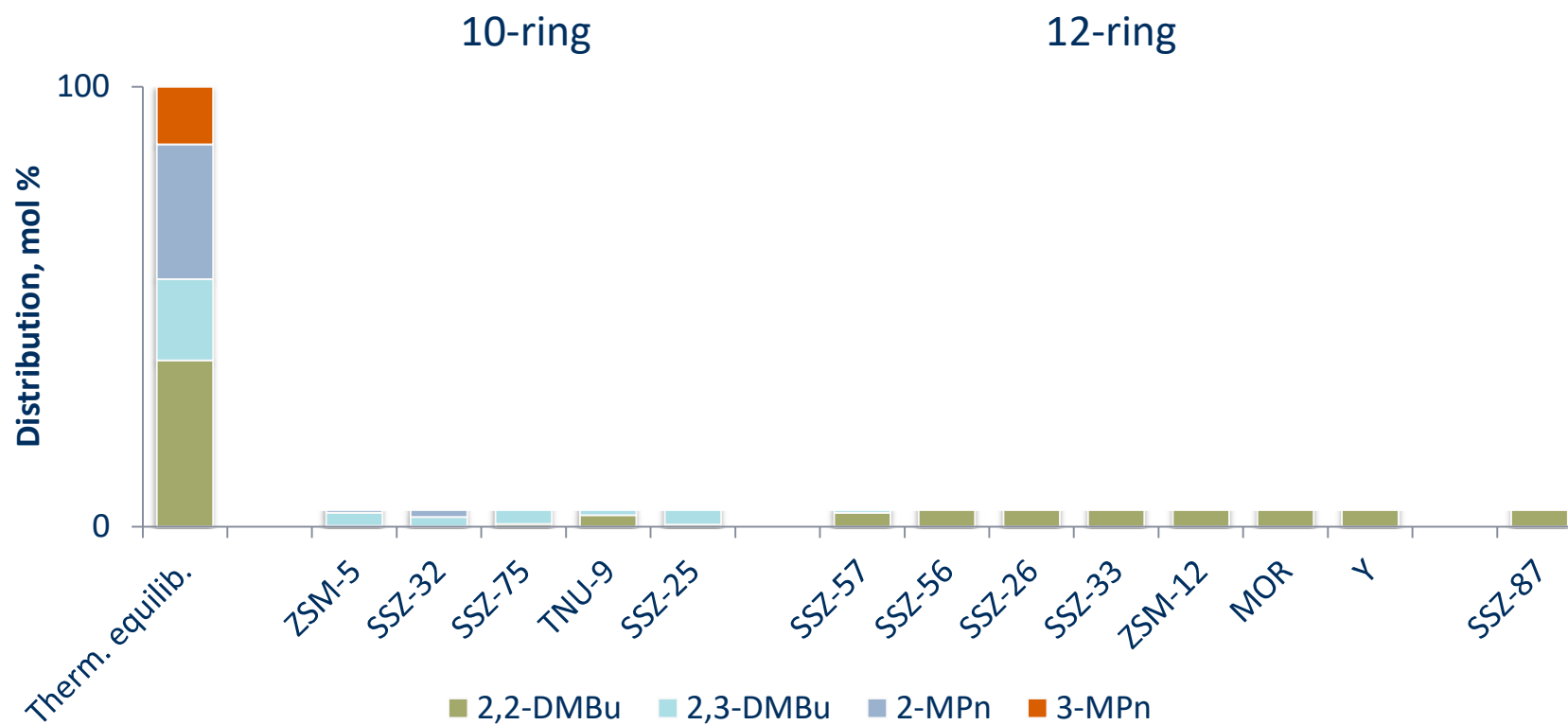
initial pH = 3

Al insertion experiments are indicative of a 12-ring zeolite!

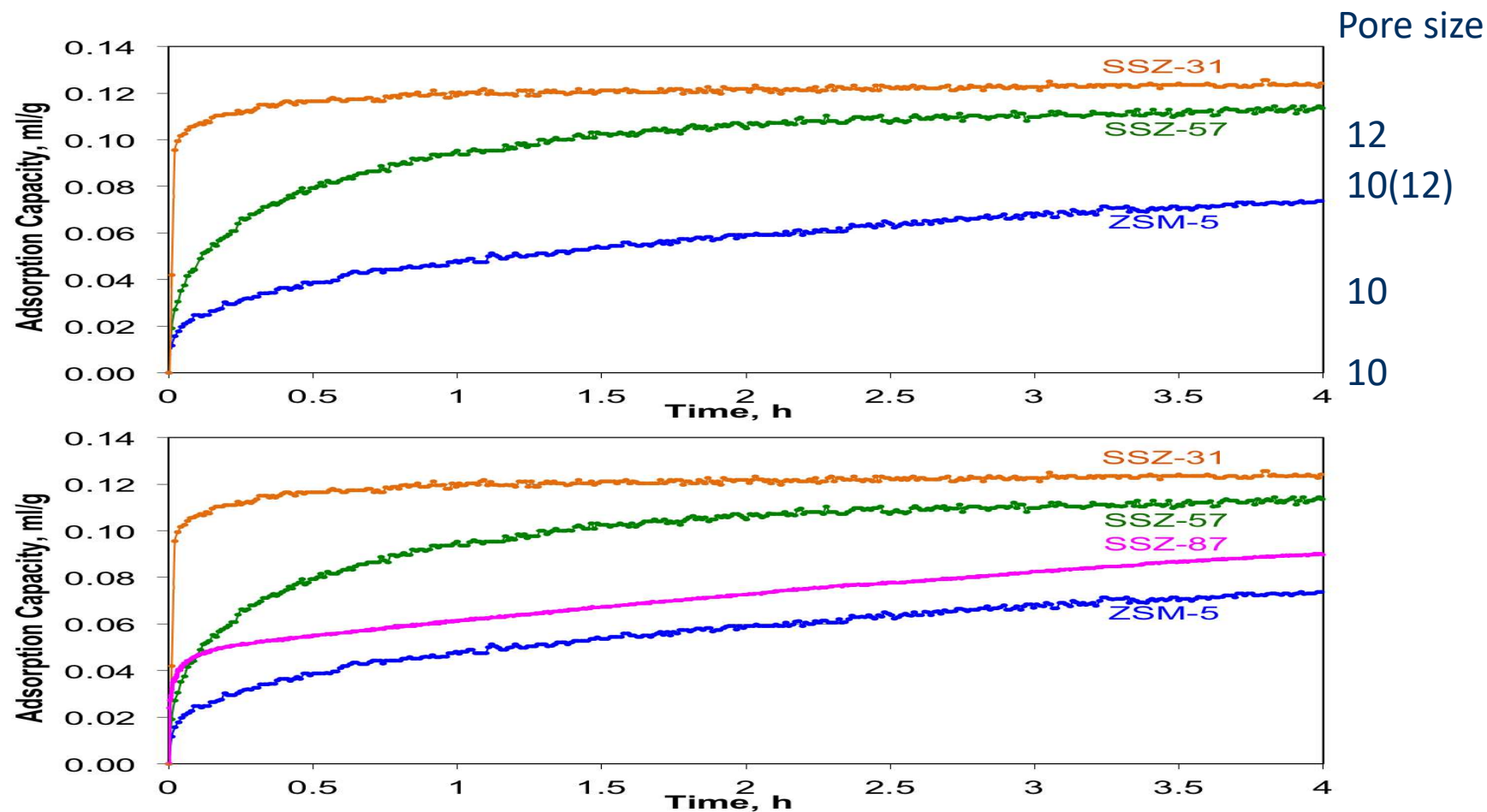


# Isomer yield experiments

Isomerisation of *n*-hexane on Pd loaded zeolites



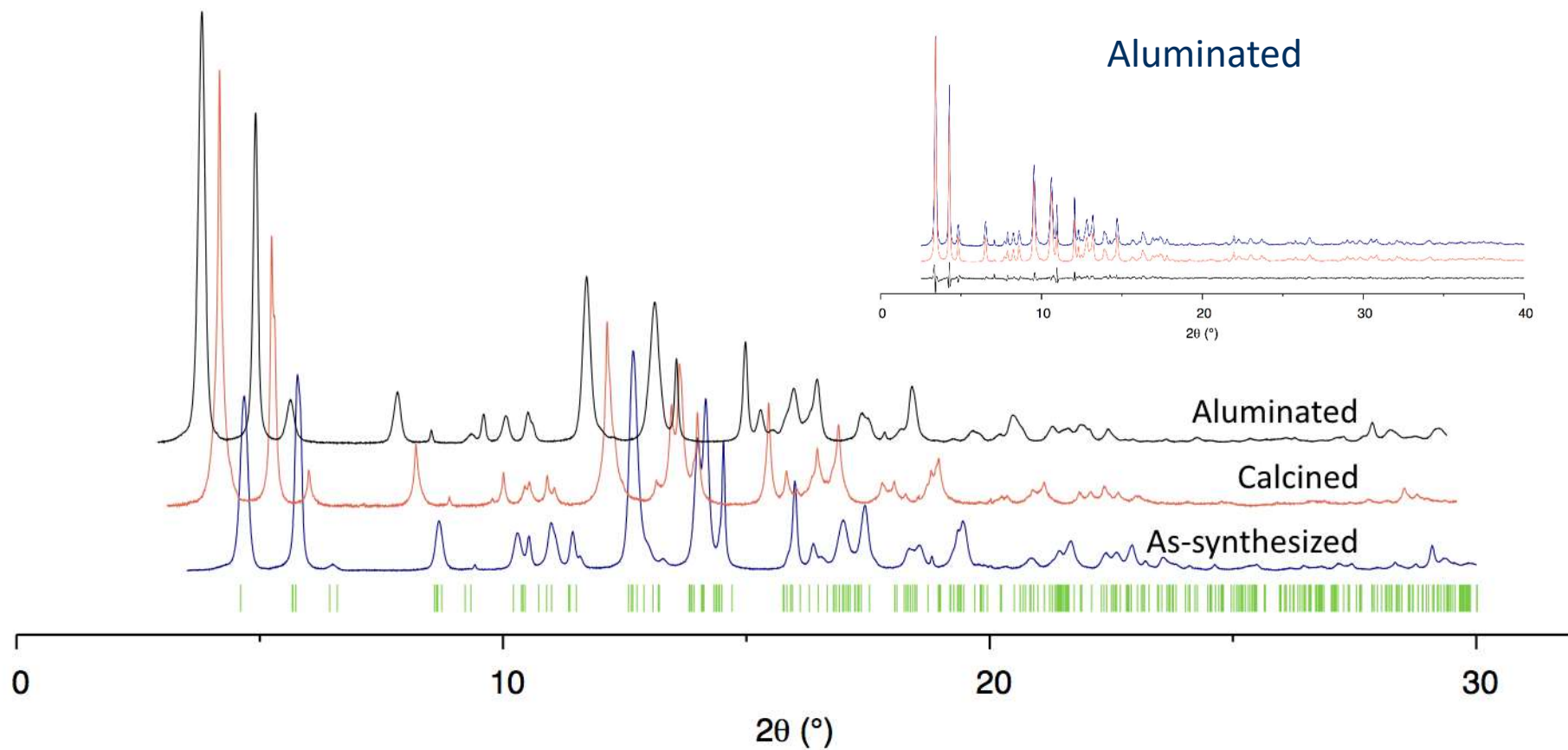
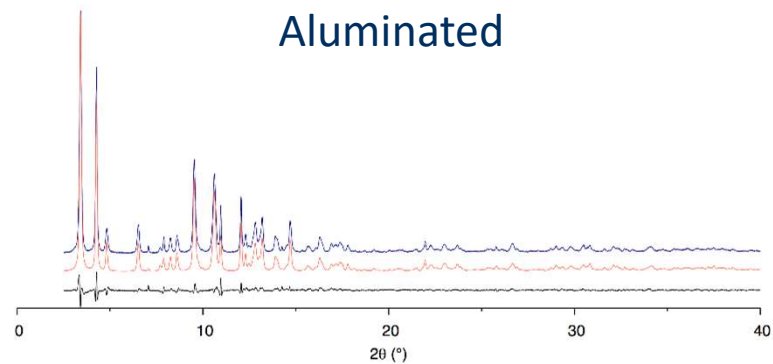
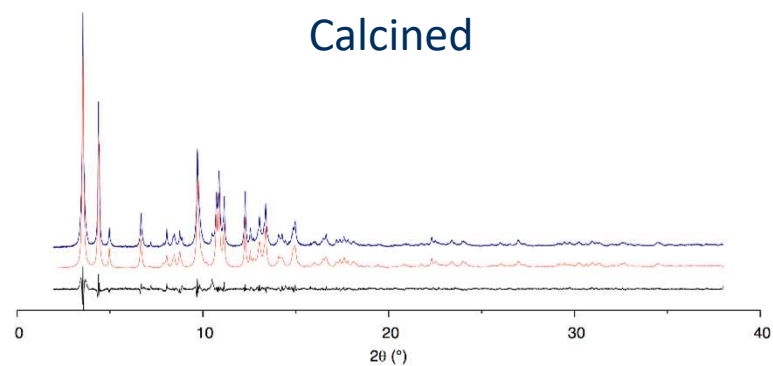
# Adsorption of 2,2-DMBu



## What is going on?

- SSZ-87 has characteristics of a large-pore zeolite
  - Al insertion
  - Isomerisation of *n*-hexane
  - Adsorption of 2,2-DMBu
- Structure determination revealed a medium-pore zeolite
  - 8 x 10-ring channel system

# XRPD of calcined/aluminated samples

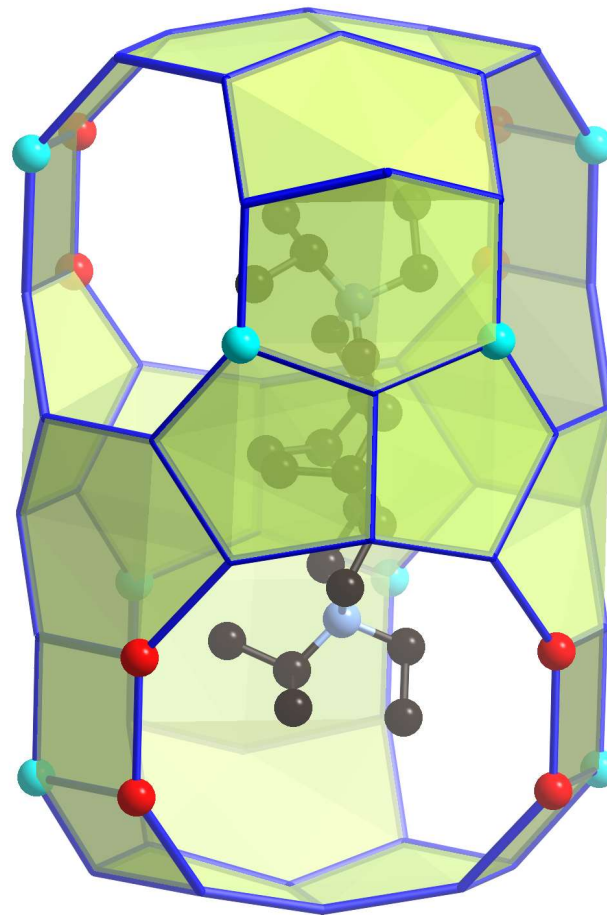


# Location of B

As-synthesized

● 0.8 Si, 0.2 B

● 0.7 Si, 0.3 B



# Location of B

As-synthesized

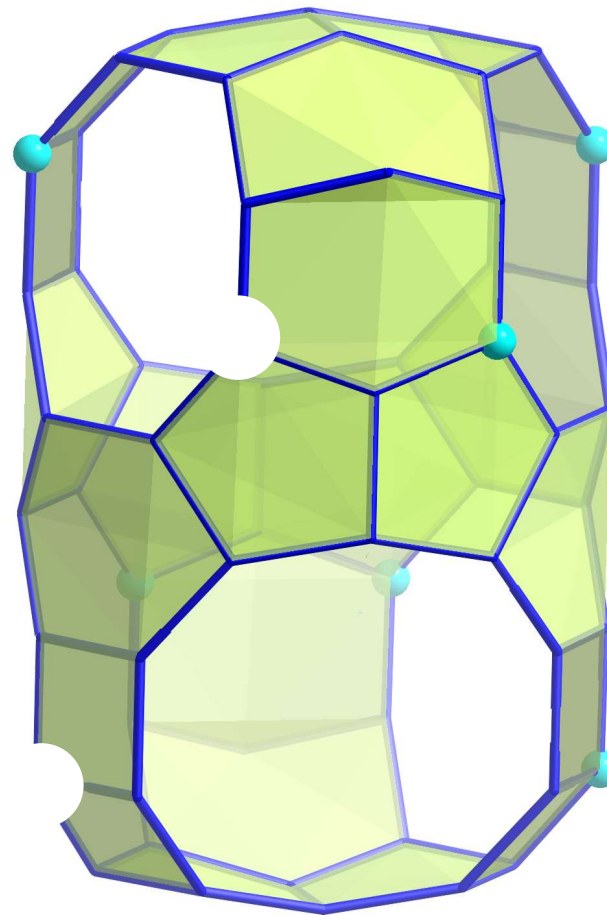
● 0.8 Si, 0.2 B

● 0.7 Si, 0.3 B

Calcined

● 1.0 Si

● 0.5 Si, 0.3 B, 0.2 □



# Location of B

As-synthesized

● 0.8 Si, 0.2 B

● 0.7 Si, 0.3 B

Calcined

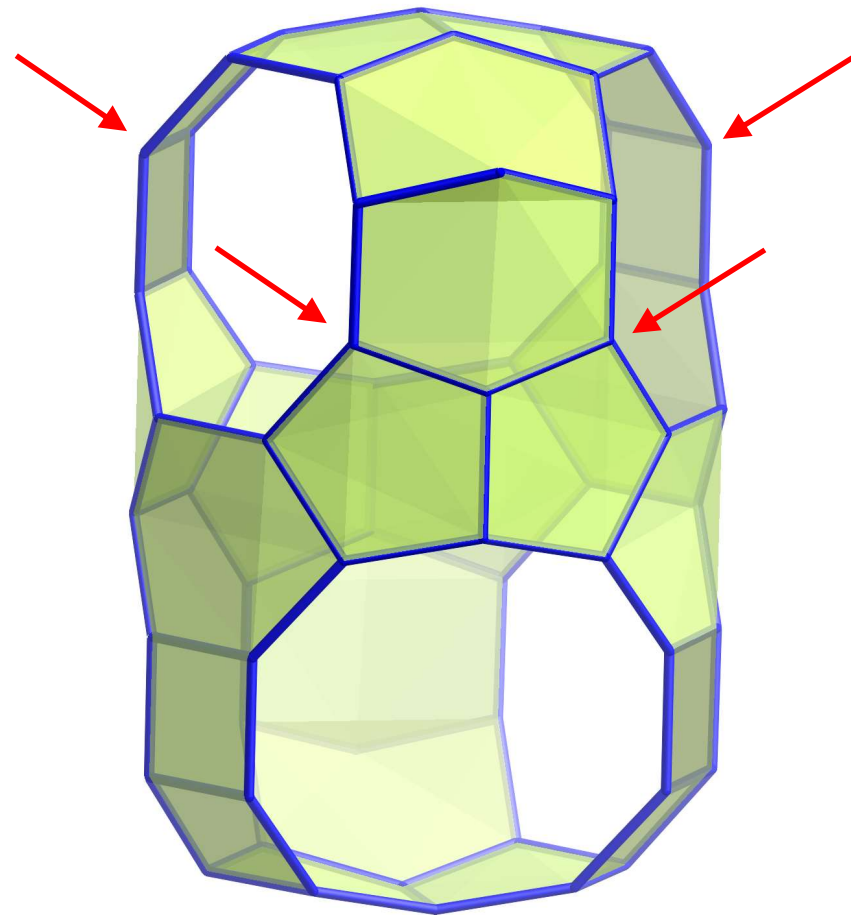
● 1.0 Si

● 0.5 Si, 0.3 B, 0.2 □

Aluminated

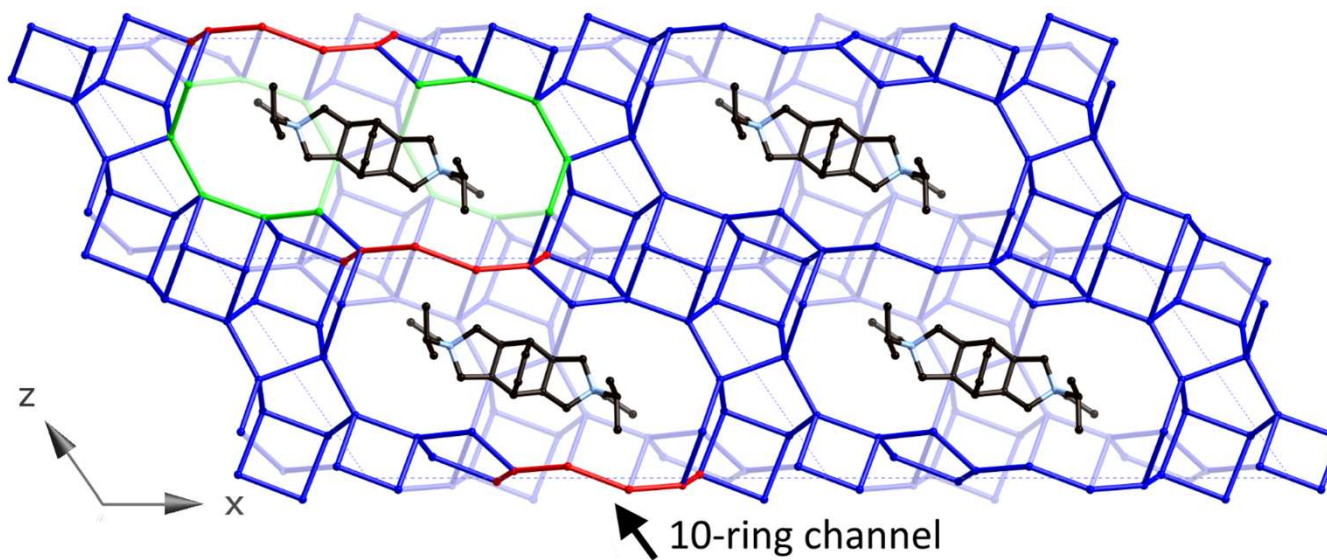
● 1.0 Al/Si

● 1.0 Al/Si



# Zeolite pore openings

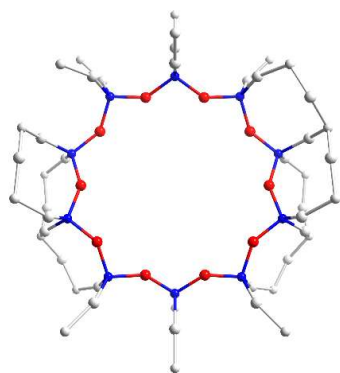
SSZ-87: Single 10-rings connecting large cages





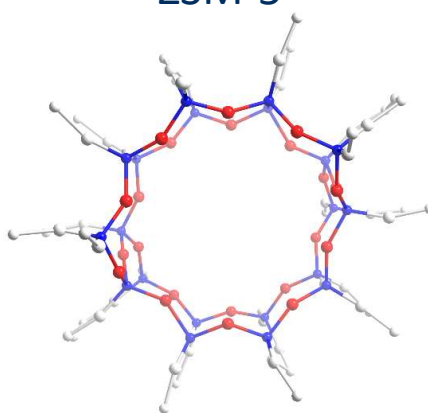
# Pore comparison

SSZ-87



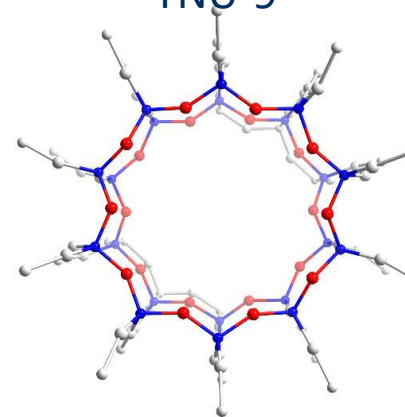
5.5 × 5.0

ZSM-5

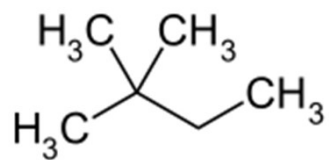


5.6 × 5.3

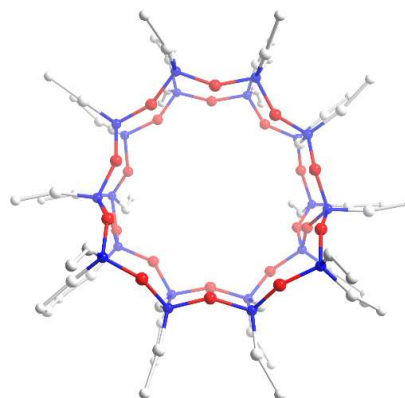
TNU-9



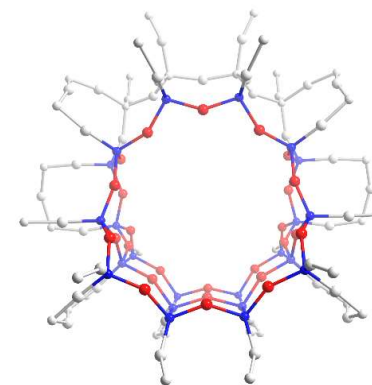
5.6 × 5.5



2,2-DMBu



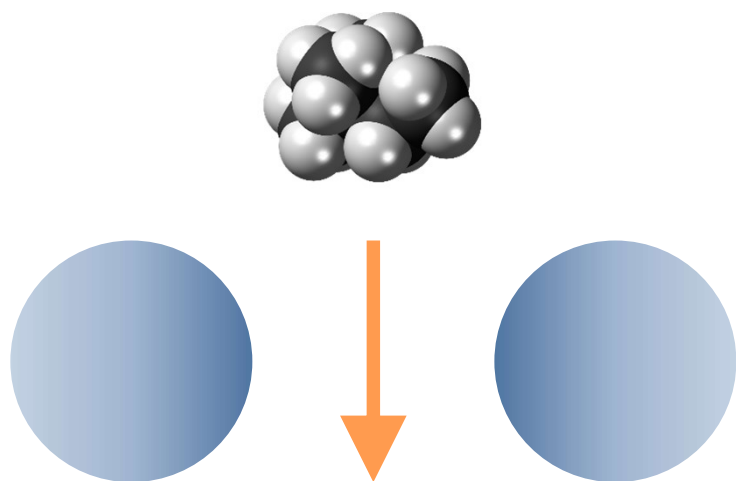
5.5 × 5.1



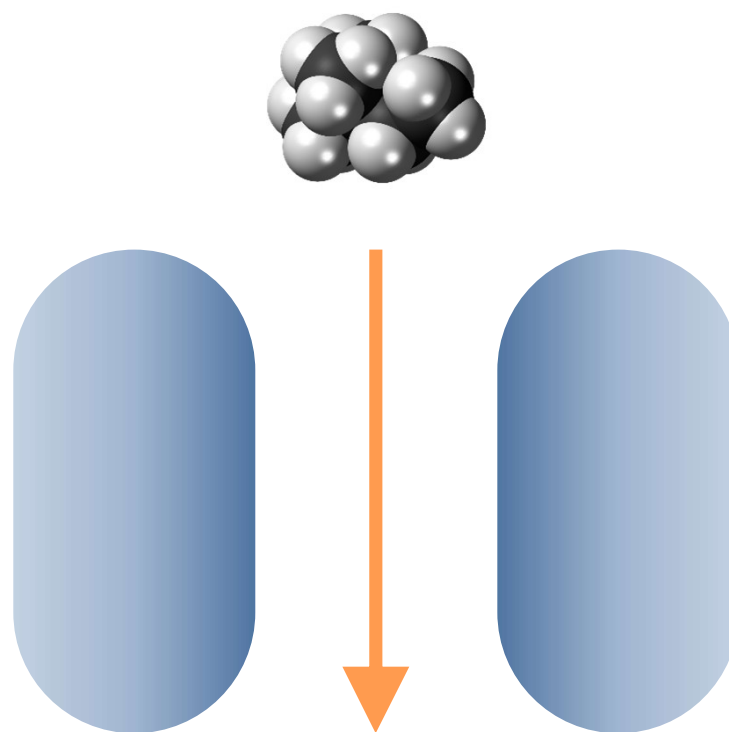
5.5 × 5.4

# Pore comparison

Single 10-ring



Double 10-ring



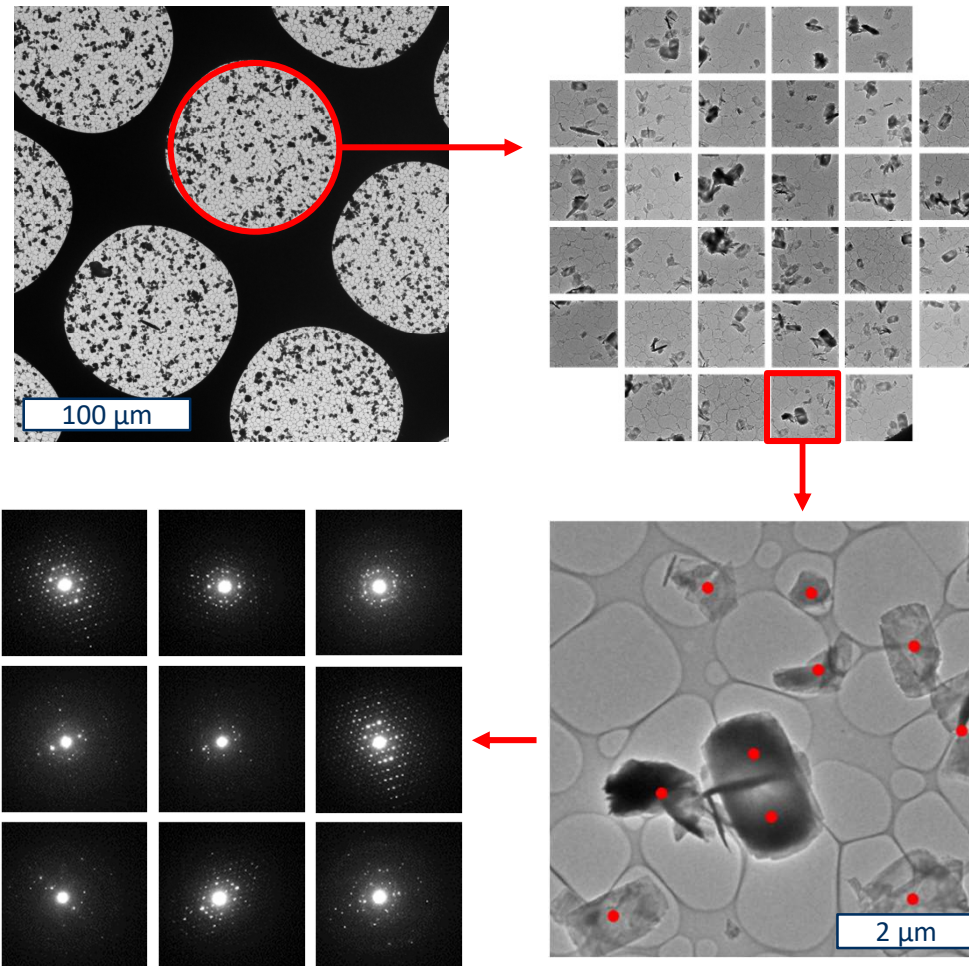
# Summary

- Structure of SSZ-87 solved by combining methods:
  - RED → Framework structure
  - XRPD → Location of B / OSDA
  - NMR → Vacancy distribution
- SSZ-87 has characteristics of a large-pore zeolite
  - ✓ Al insertion
  - ✓ Isomerisation of *n*-hexane
  - ✓ Adsorption of 2,2-DMBu
- Unique characteristics inbetween a 10- and 12-ring zeolite

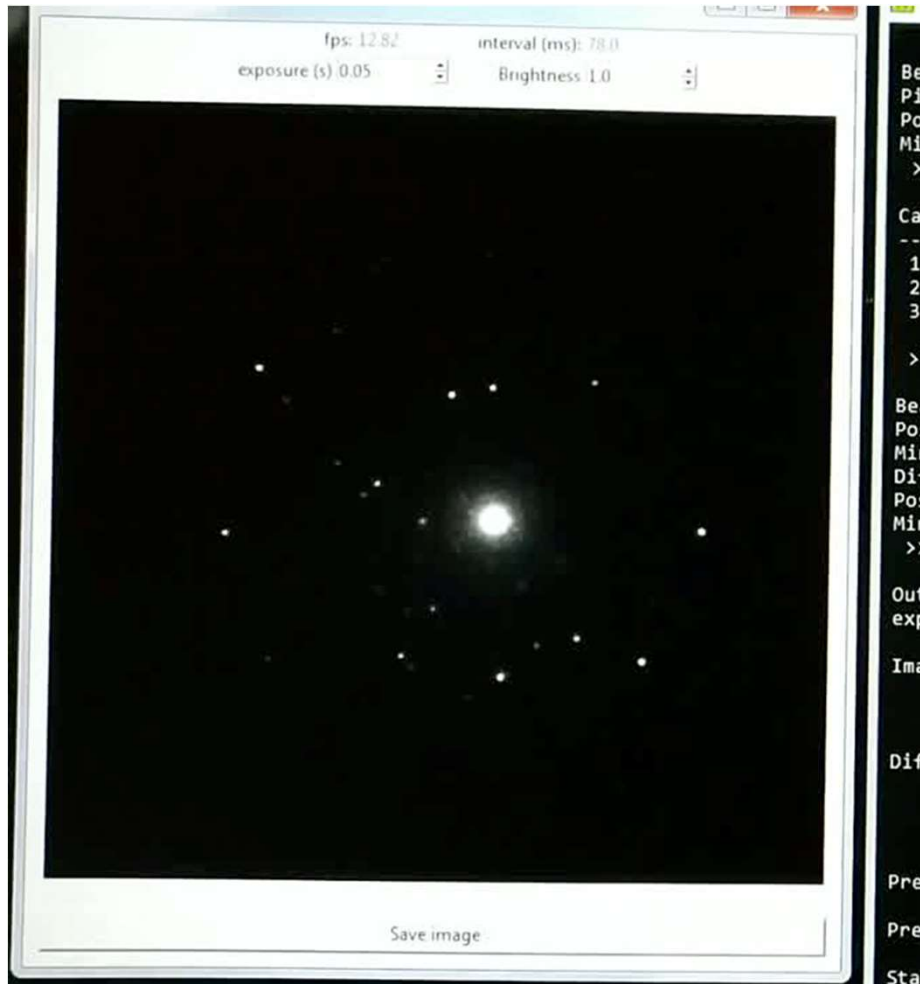
# Serial electron diffraction

S. Smeets & W. Wan,  
*In manuscript.*

# Serial electron diffraction



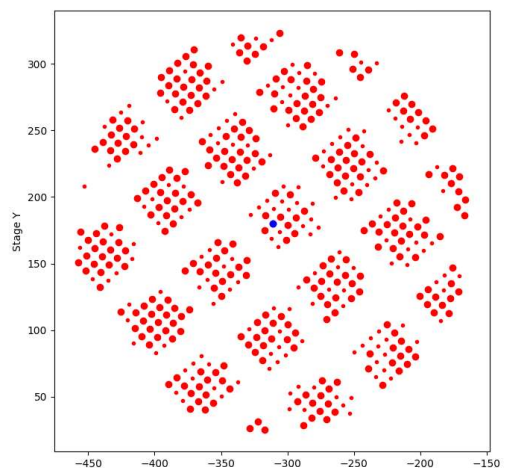
# Automated data collection



- Collect 3000 patterns/hr
- Zeolite Na-Y  
(Synthesis by Yi Luo,  
Stockholm Univ.)

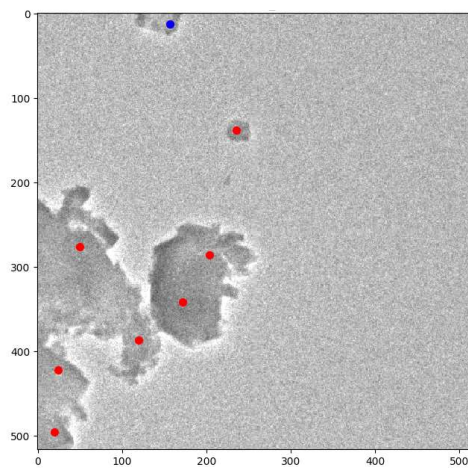
# Zeolite Na-Y

Stage map



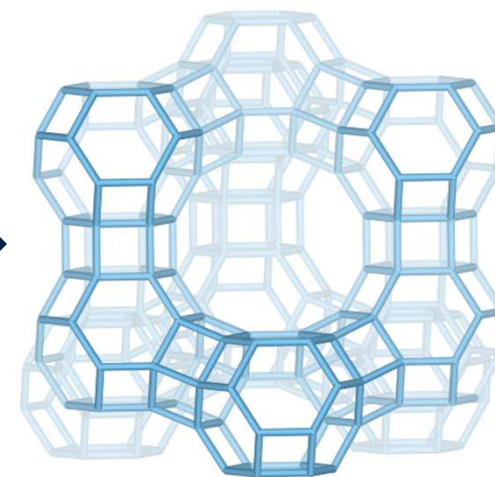
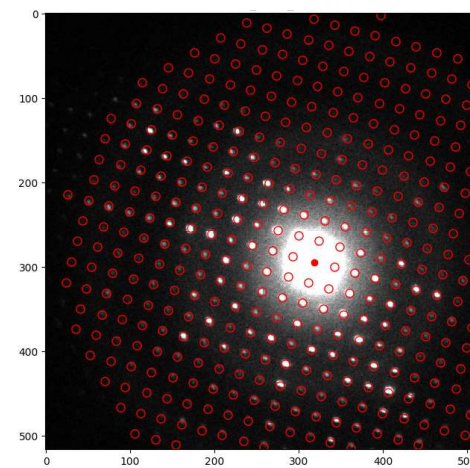
200 x 200  $\mu\text{m}$

Locate crystals



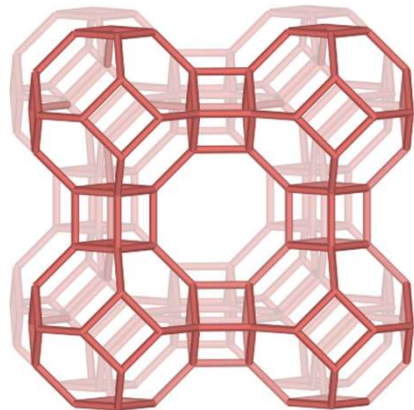
6 x 6  $\mu\text{m}$

Diffraction

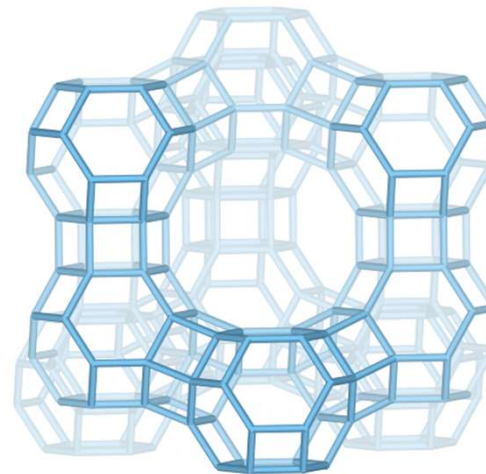


# Applications

- Structure determination (of beam-sensitive materials)
- Screening
- Phase analysis
- Structures solved:



Zeolite A (**LTA**)

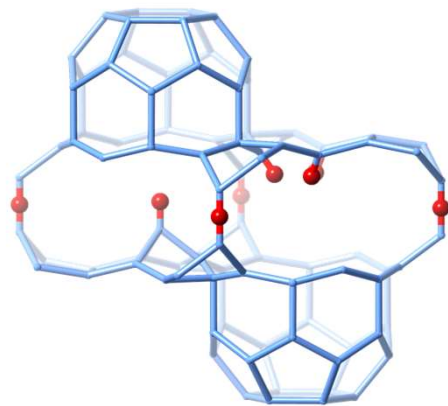


Zeolite Y (**FAU**)

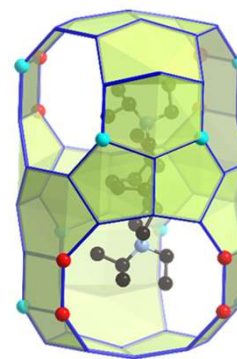


# Conclusions

- Any one method does not contain all information
- Rely on XRPD for structure confirmation
- Borrow from other methods to supplement XRPD
- Serial electron diffraction will offer new possibilities for structure analysis



SSZ-70



SSZ-87