

Oorgan, Nynäshamn, SE  
13-06-2017

# The structure of zeolite SSZ-70 through combined HRTEM, XRPD, and DNP-enhanced 2D NMR

Stef Smeets



SWISS NATIONAL SCIENCE FOUNDATION

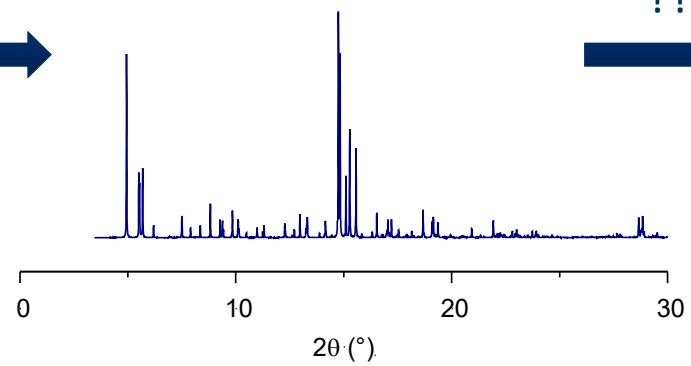


Stockholm  
University

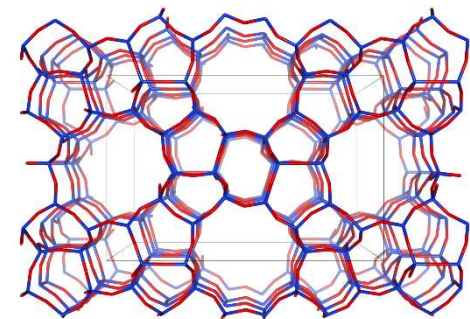
# Structure determination



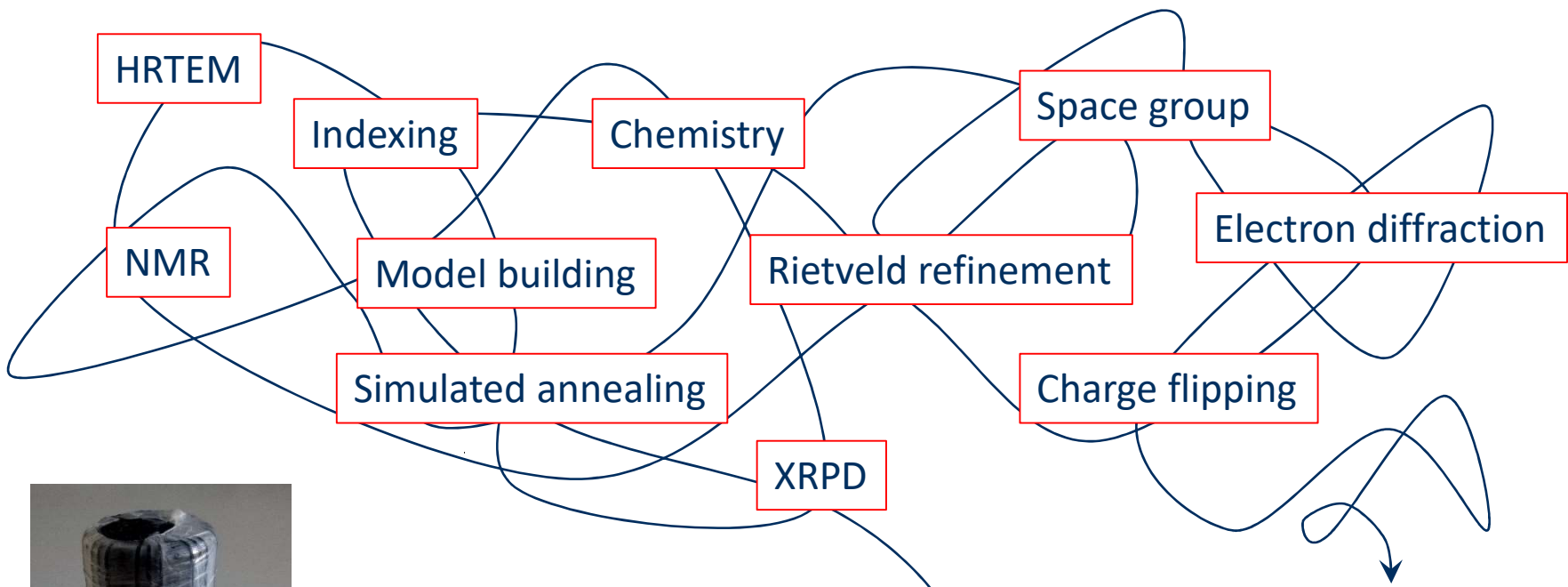
Sample



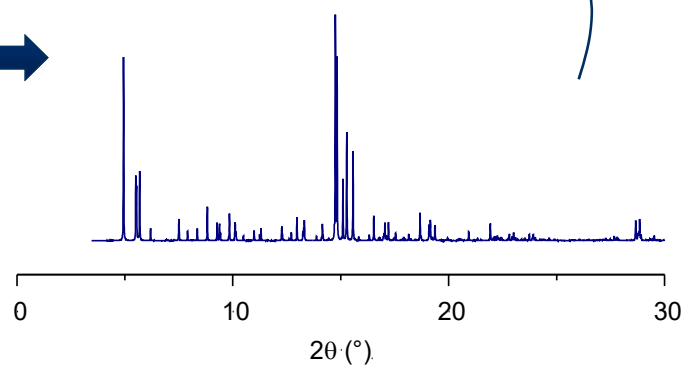
Characterize



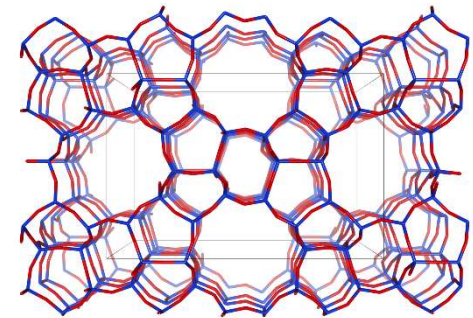
Structure



Sample



Characterize



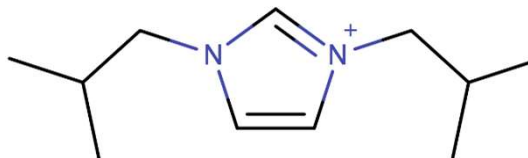
Structure

# Zeolite SSZ-70

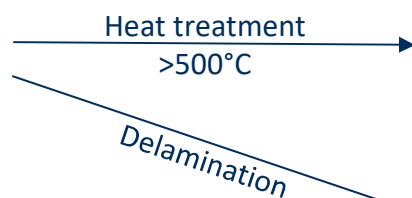
Stacey Zones and Alan Burton,  
US Patent 7,108,843 B2, 2006

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

Structure-directing agent

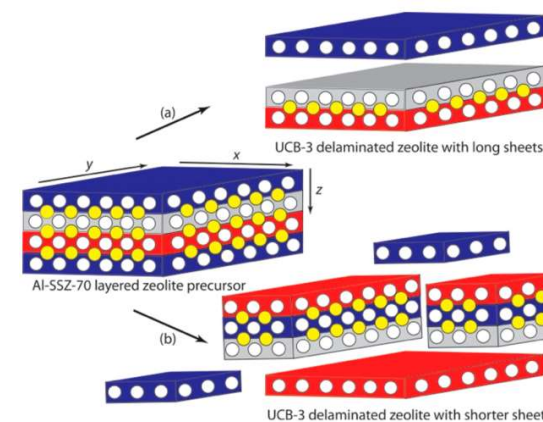


Pure silicate  
Borosilicate  
Aluminosilicate

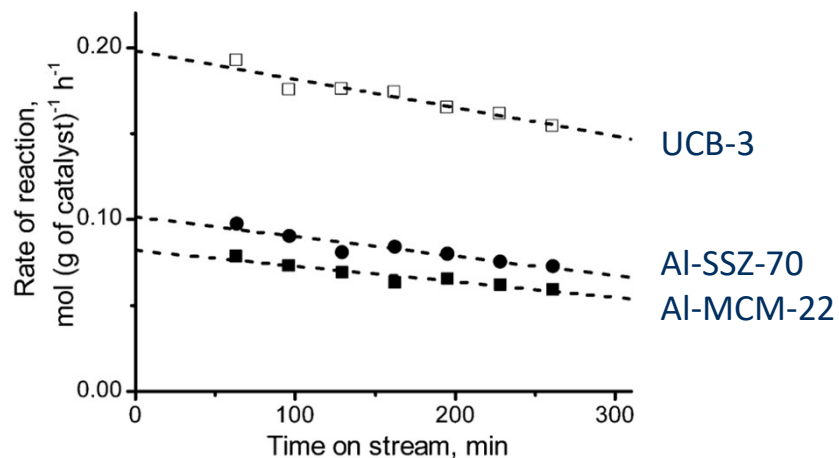


Calcined  
SSZ-70

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



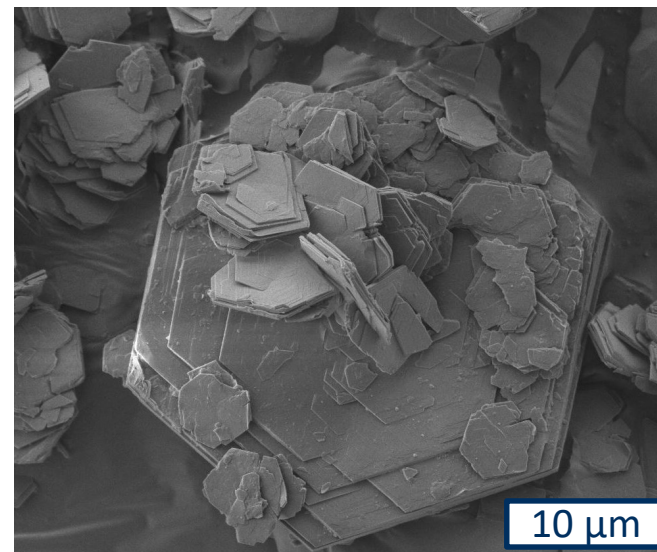
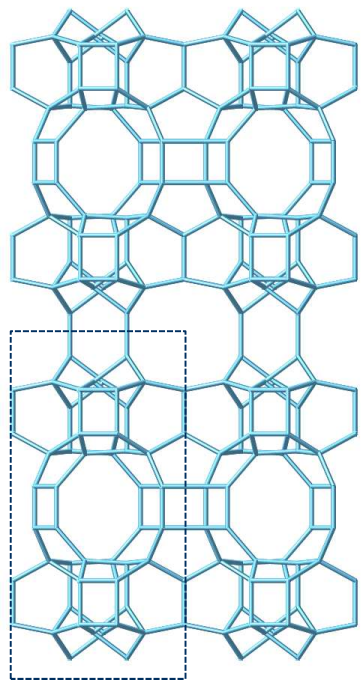
Catalysis: aromatic alkylation



Runnebaum *et al.*, 2014, *ACS Catal.*, 4, 2364

# As-made Si-SSZ-70

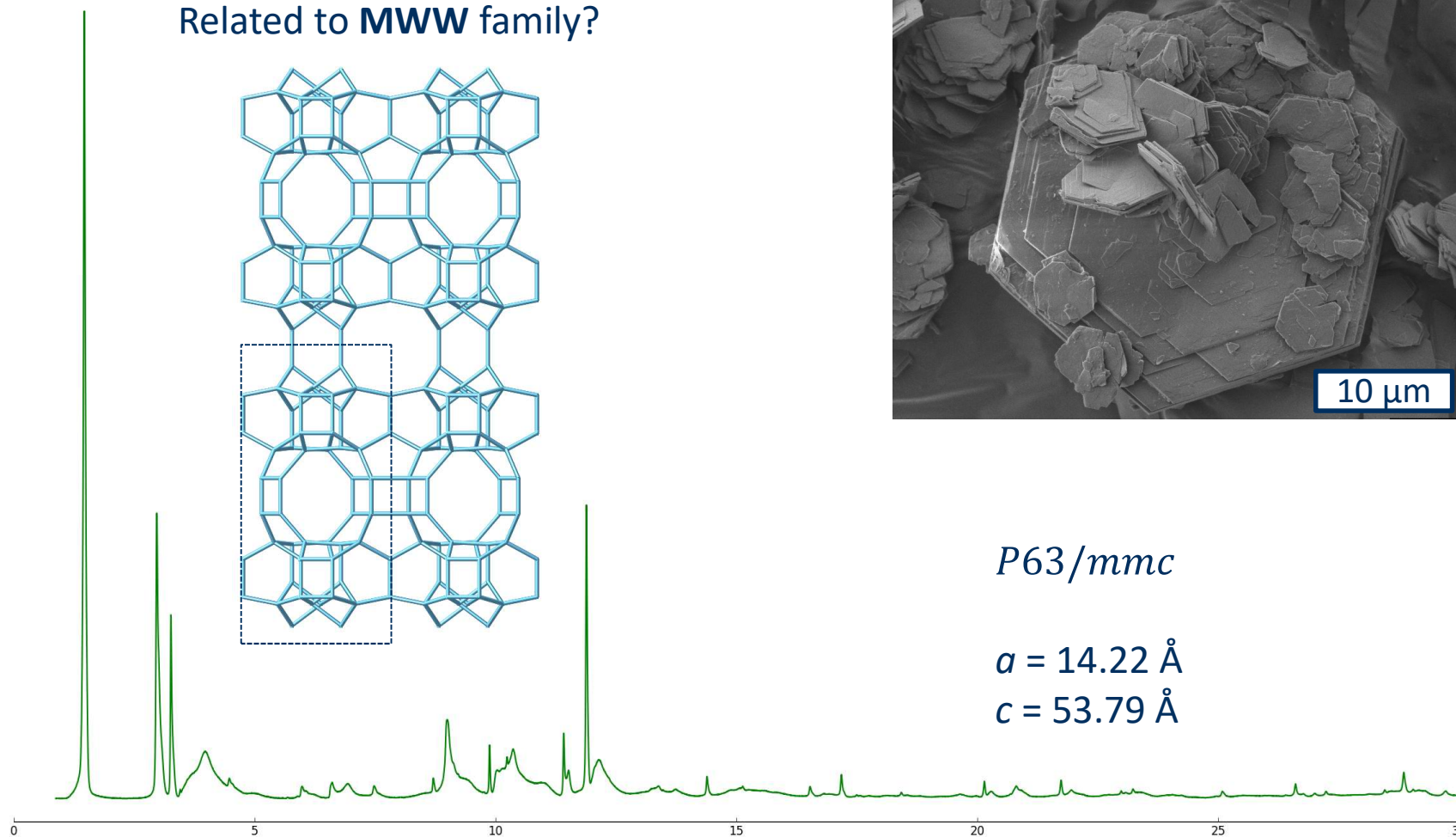
Related to **MWW** family?



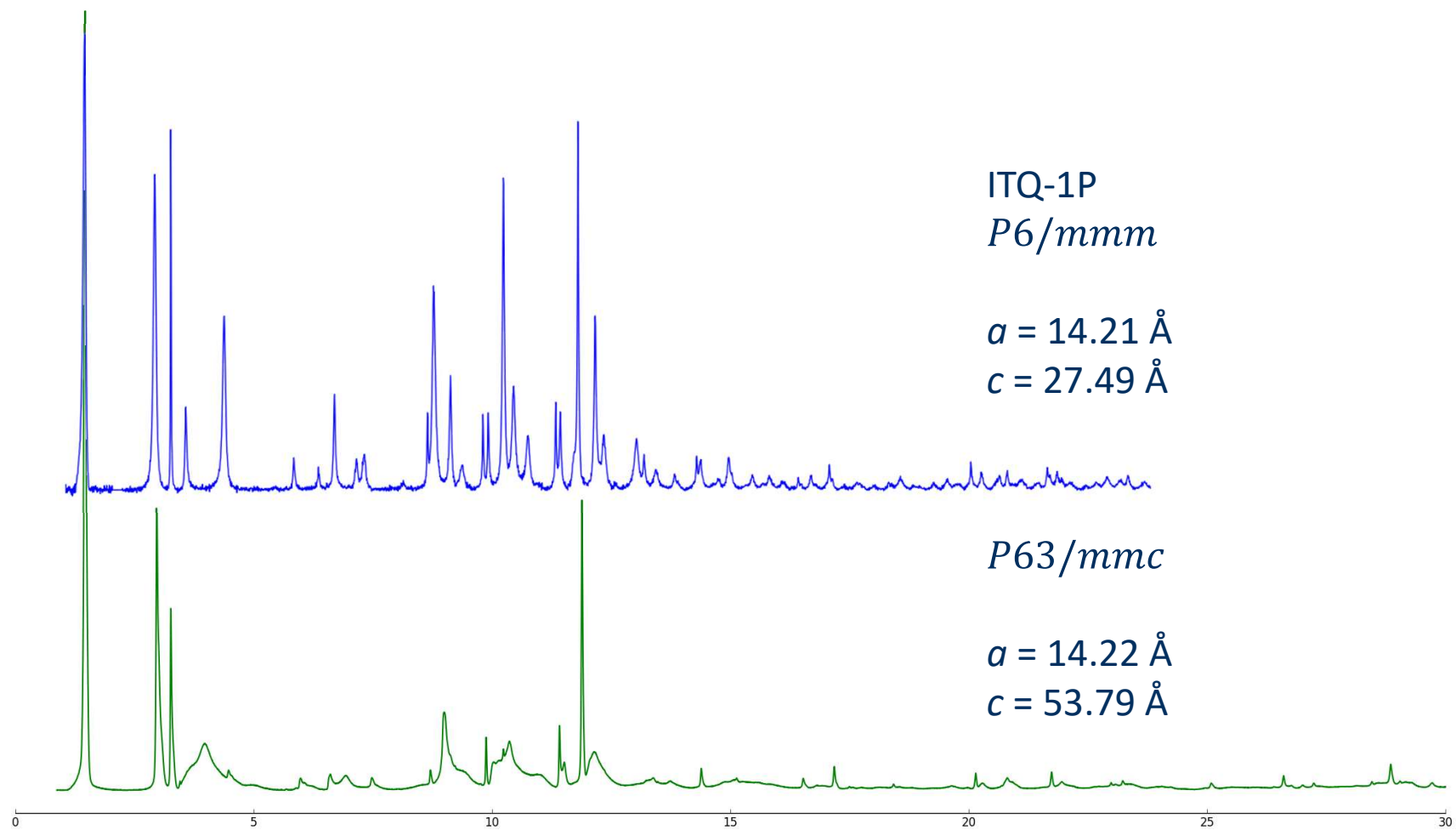
$P63/mmc$

$a = 14.22 \text{ \AA}$

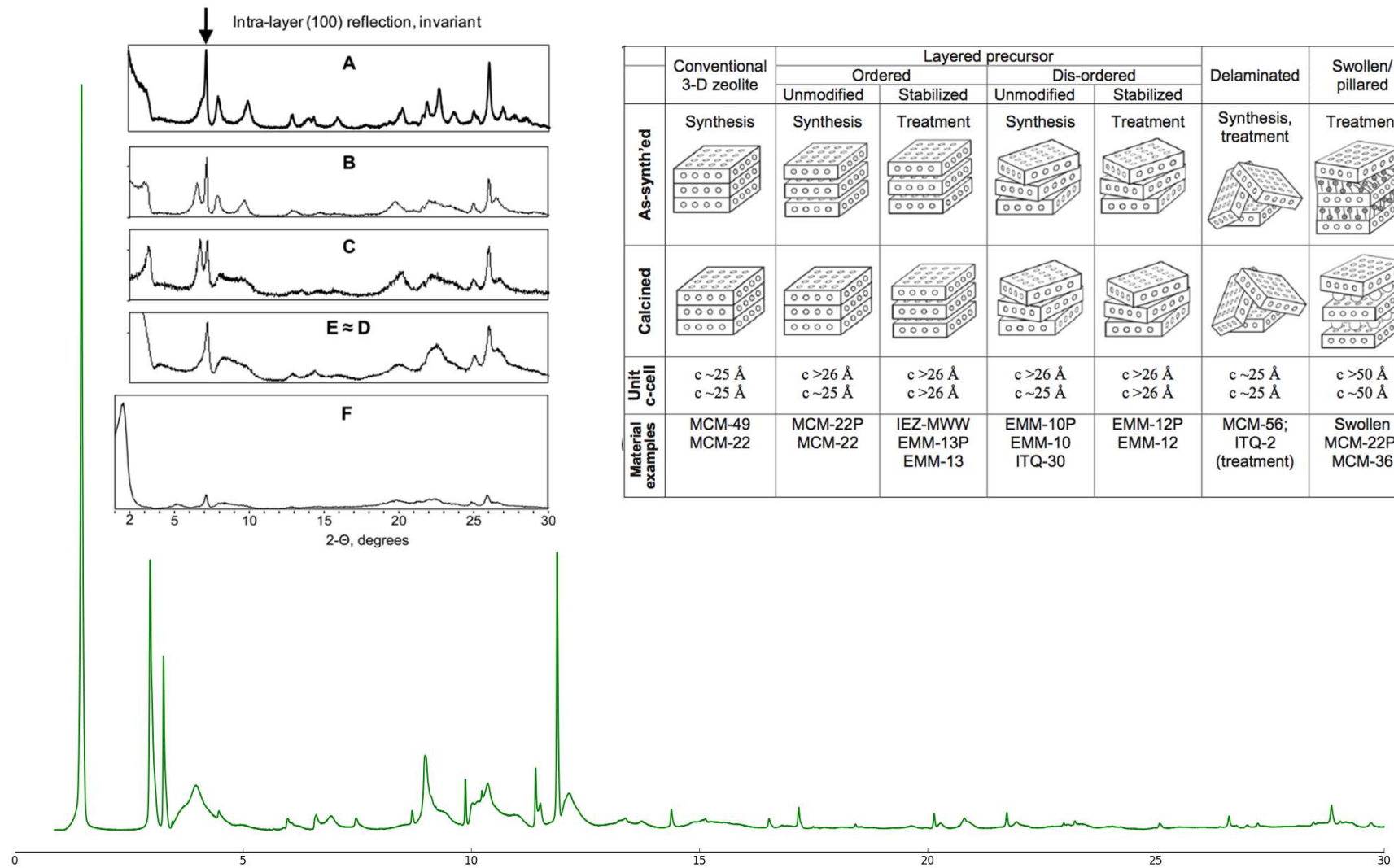
$c = 53.79 \text{ \AA}$



# As-made Si-SSZ-70



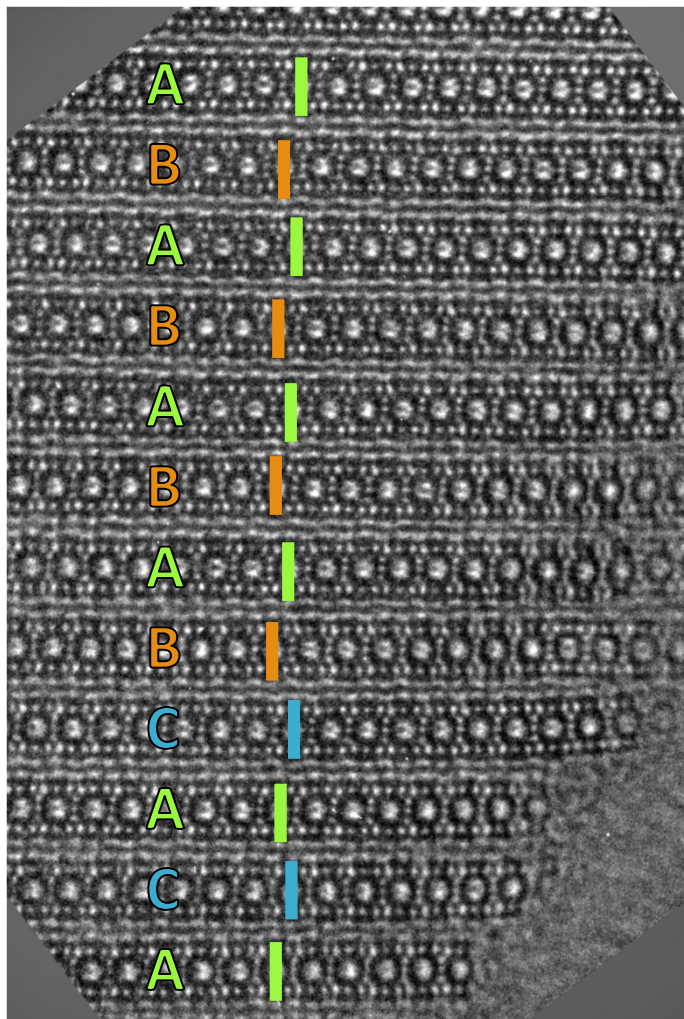
# As-made Si-SSZ-70





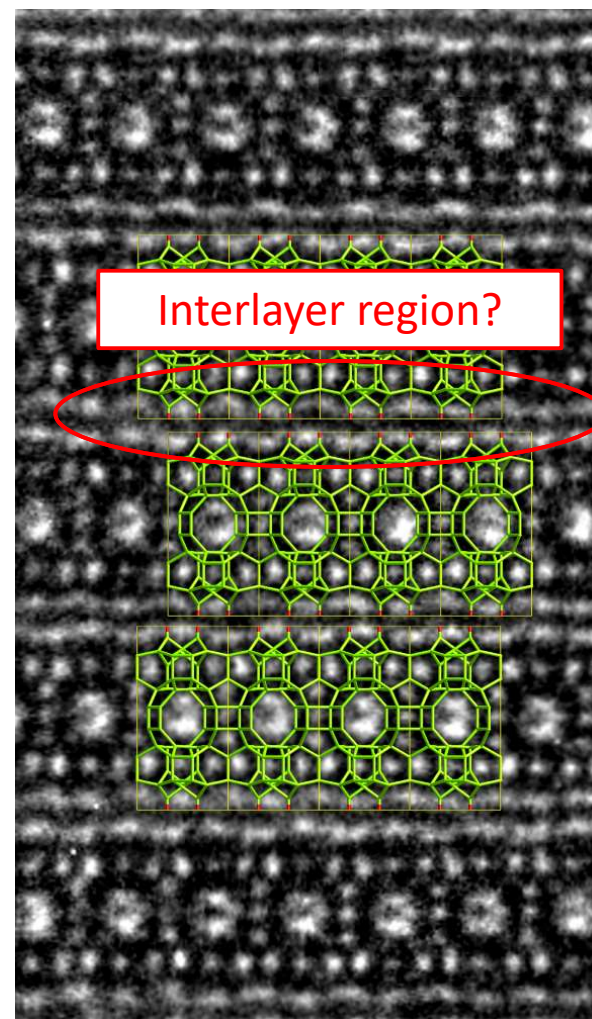
# HRTEM

Stacking disorder along [001]



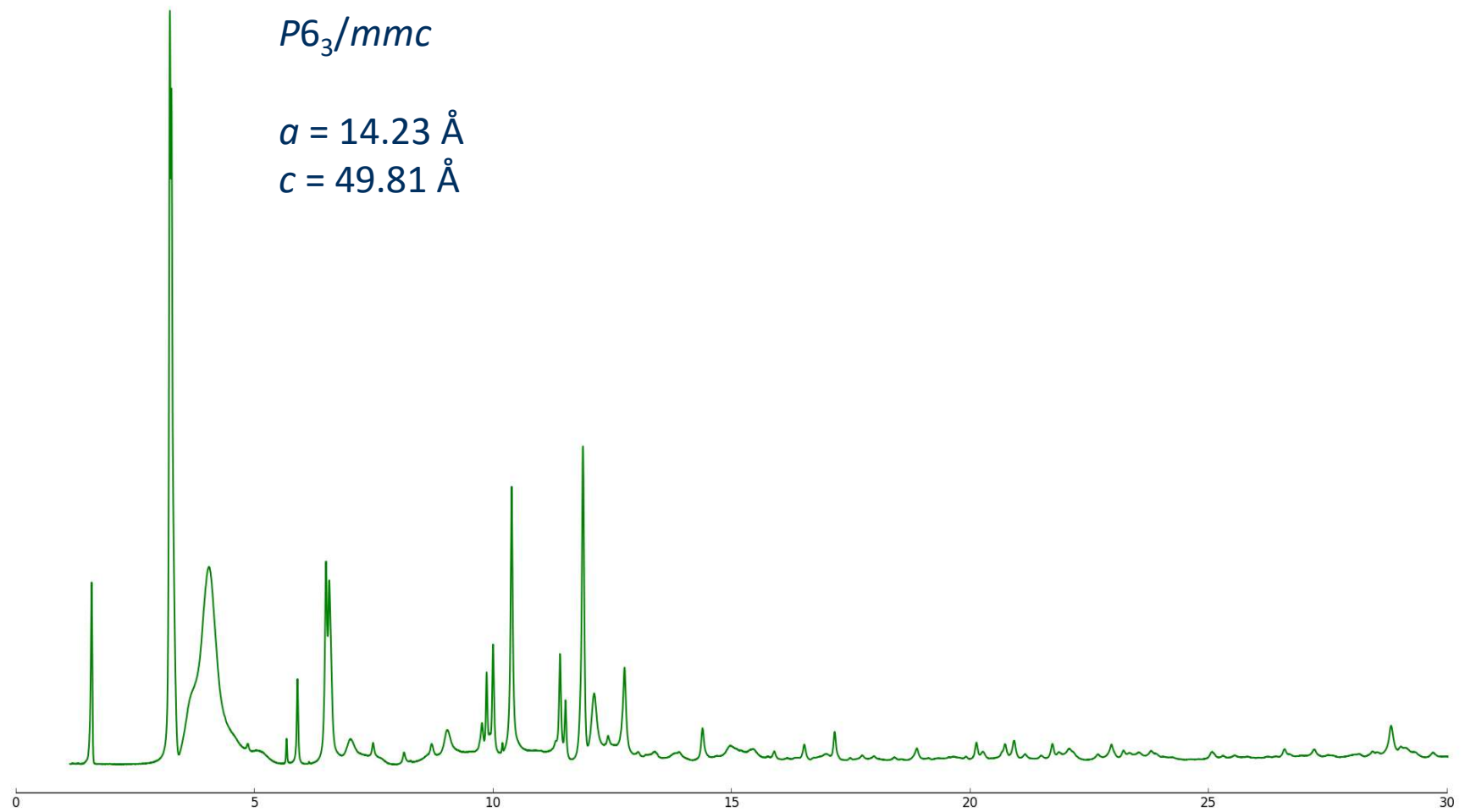
Collected by Wei Wan, Stockholm University, SE

MWW-layers





# Calcined Si-SSZ-70



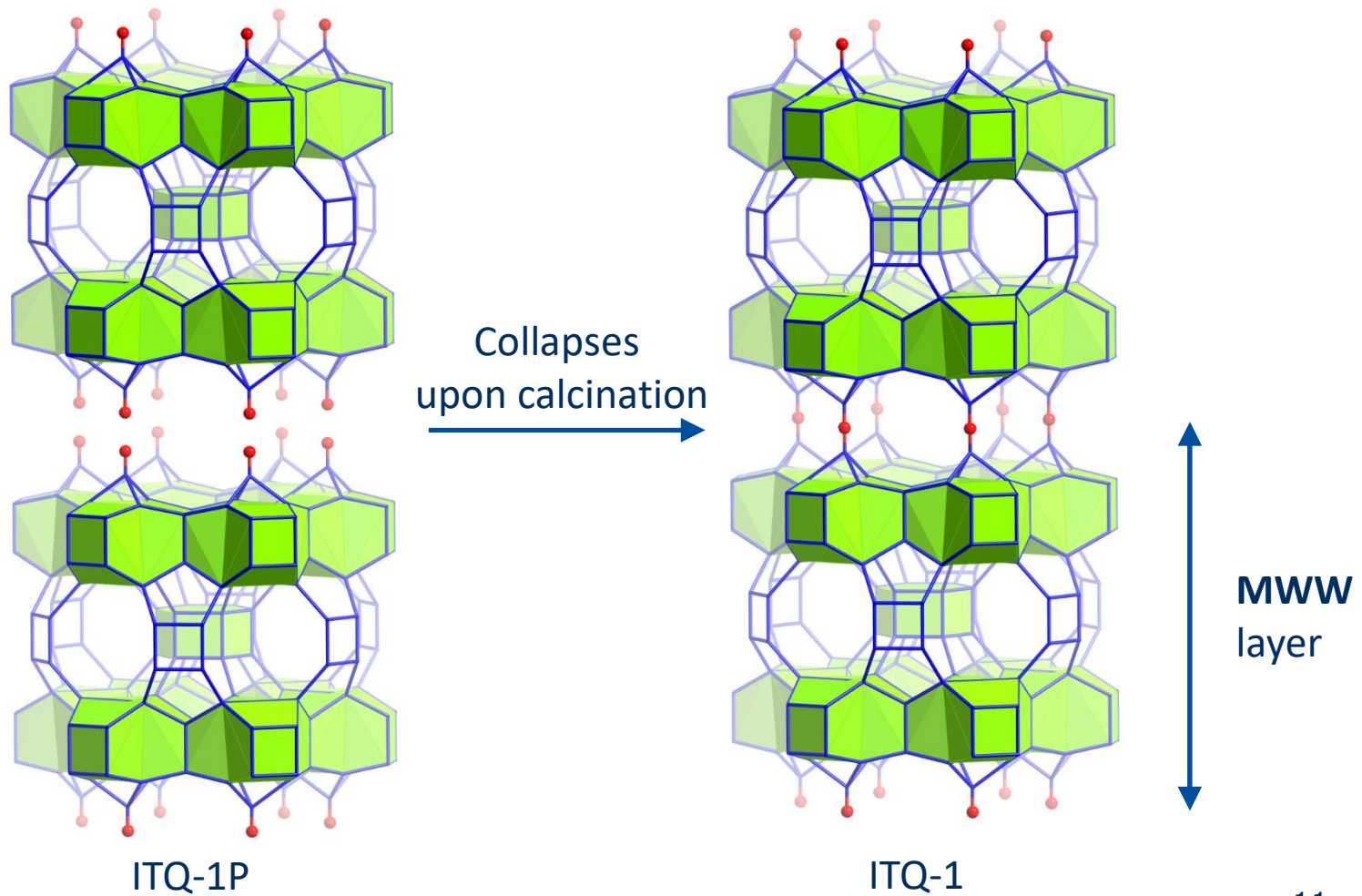
# Unit cell parameters

Zeolite	Space group	$a$ (Å)	$c$ (Å)
ITQ-1P	$P6/mmm$	14.21	27.49
ITQ-1 (MWW)	$P6/mmm$	14.21	24.94
SSZ-70 (as-made)	$P63/mmc$	14.22	53.79
SSZ-70 (calcined)	$P63/mmc$	14.23	49.81

ITQ-1P: Njo, **1998**, *PhD thesis*

ITQ-1: Cambor *et al.*, **1998**, *J. Phys. Chem. B*, 102, 44

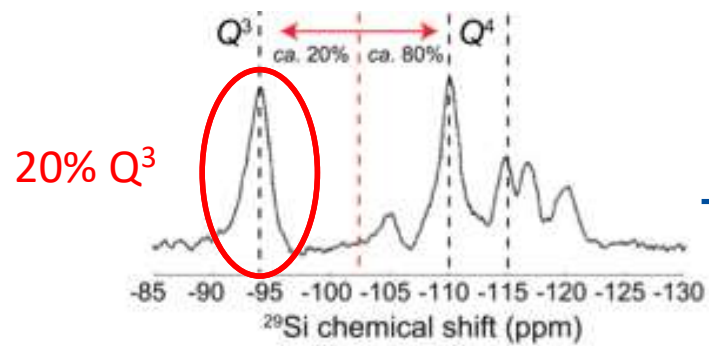
# ITQ-1 (MWW)



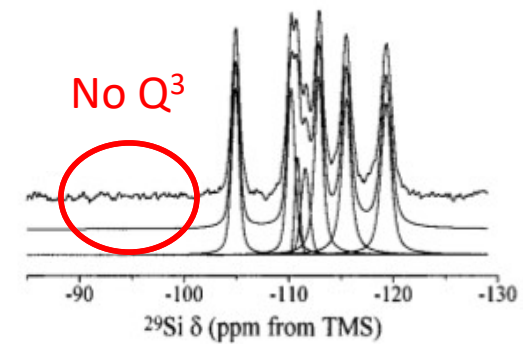
# Solid-state $^{29}\text{Si}$ MAS NMR

As-made

Calcined



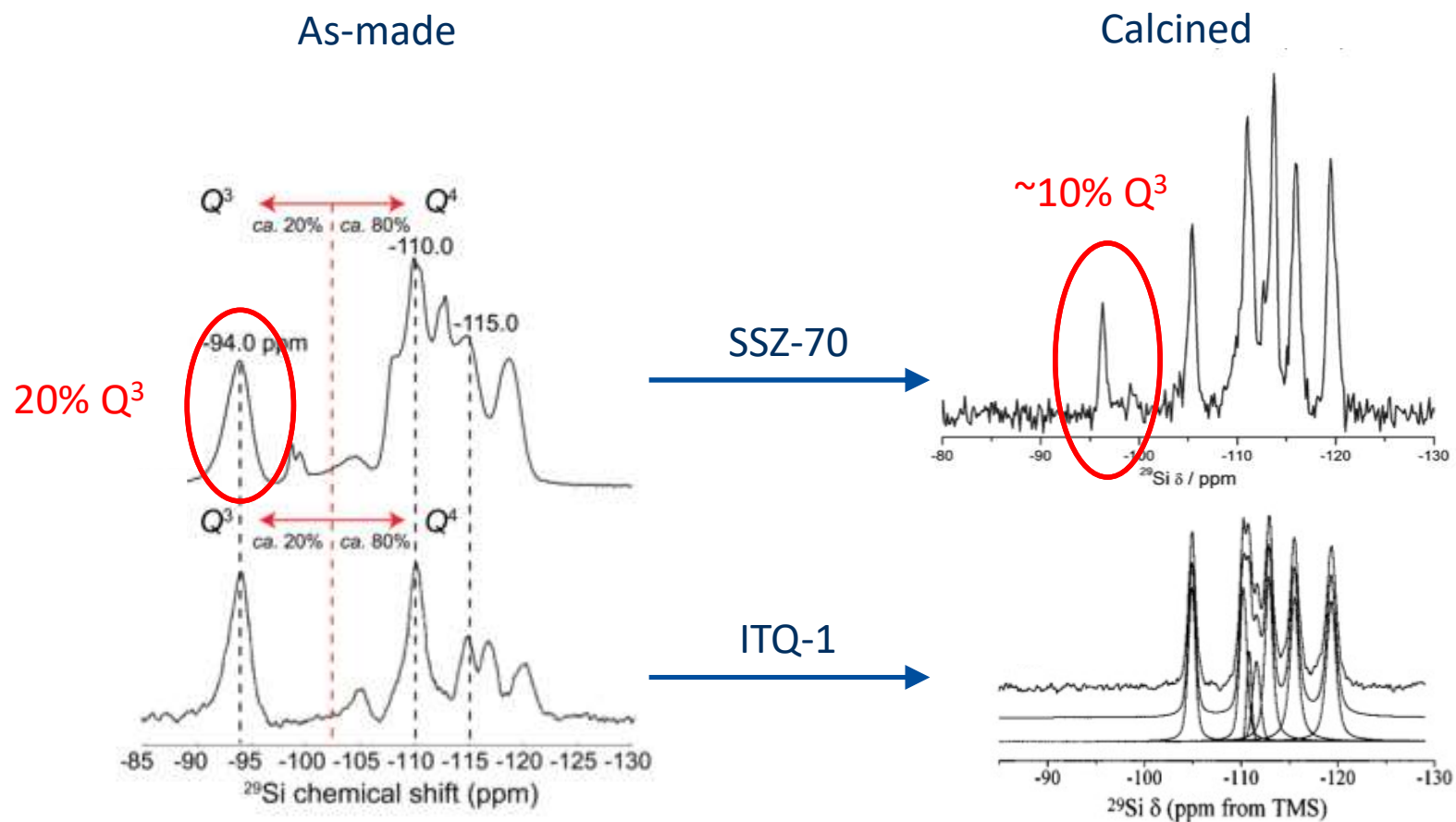
ITQ-1



Hsieh, Aronson and Chmelka (2014)

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

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

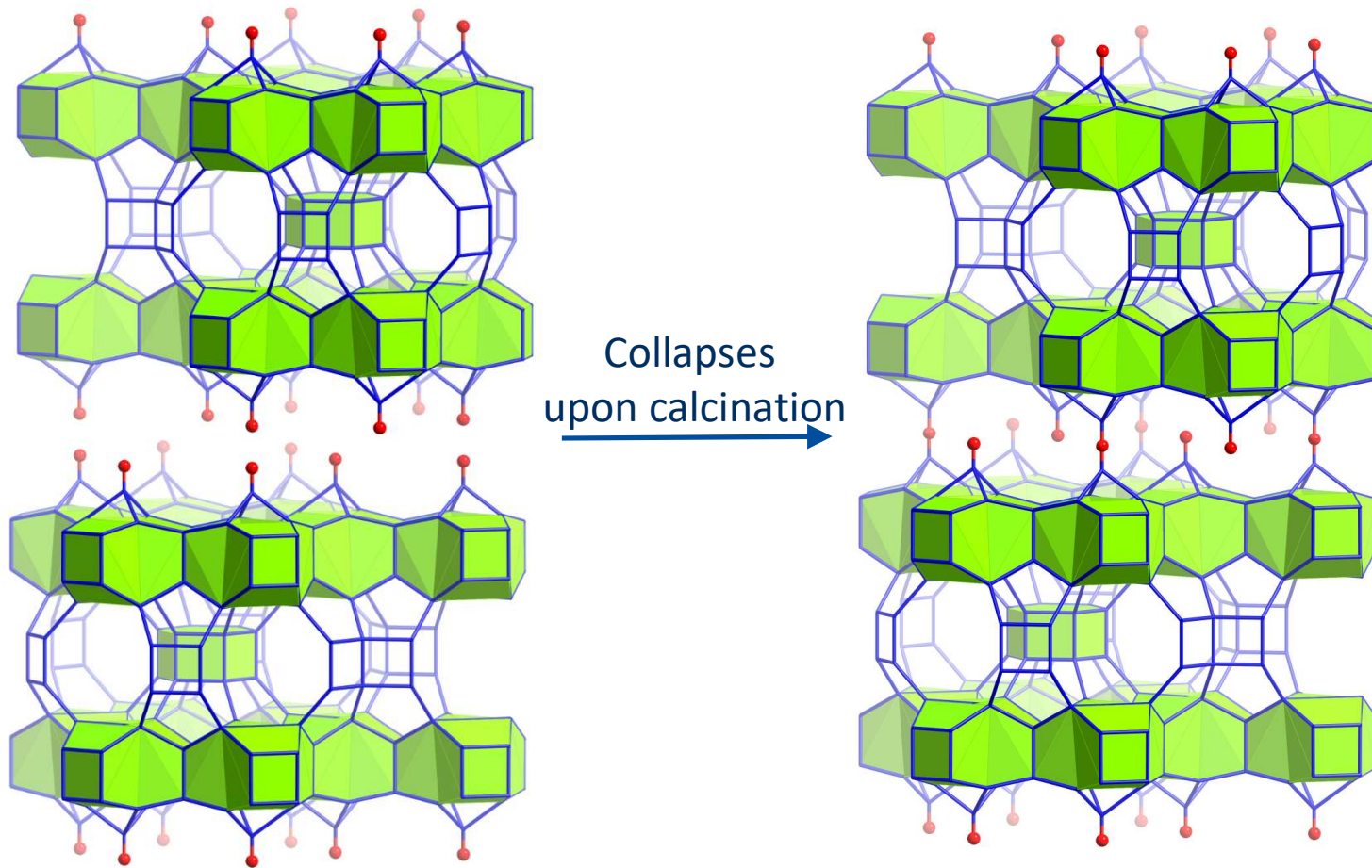


Hsieh, Aronson and Chmelka (2014)

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



# Model for SSZ-70



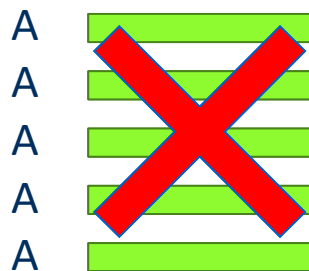
As-made SSZ-70

Calcined SSZ-70

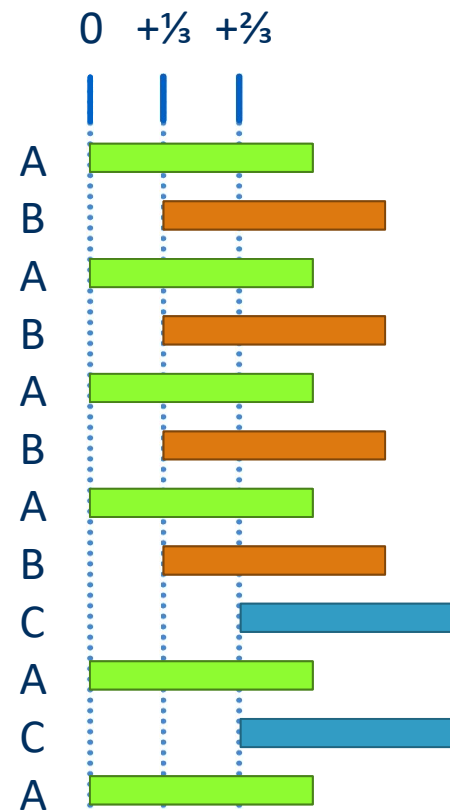
# Disorder model

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

$P(A \rightarrow A) = 0\%$   
 $P(A \rightarrow B) = 50\%$   
 $P(A \rightarrow C) = 50\%$

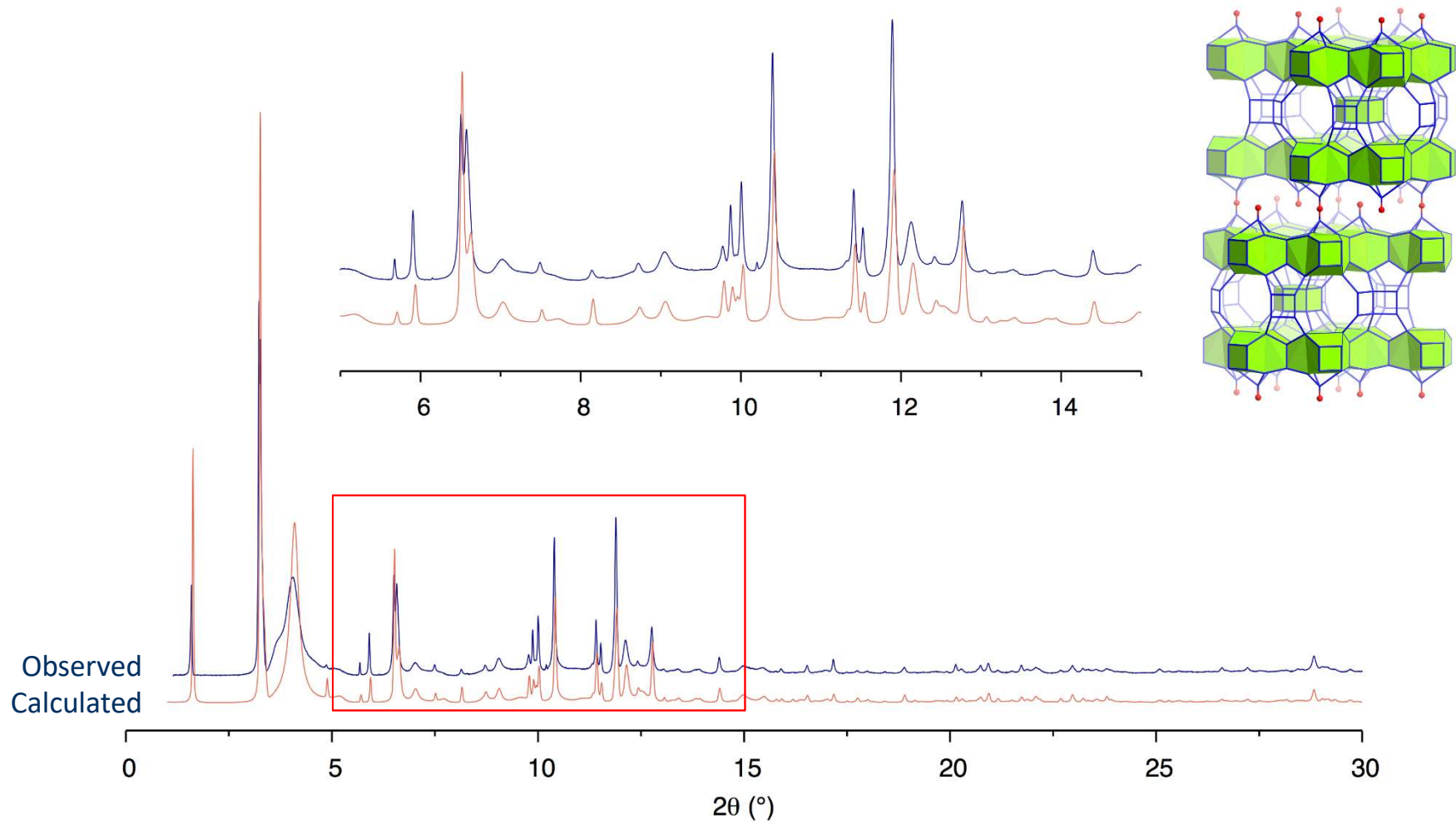


**ITQ-1**

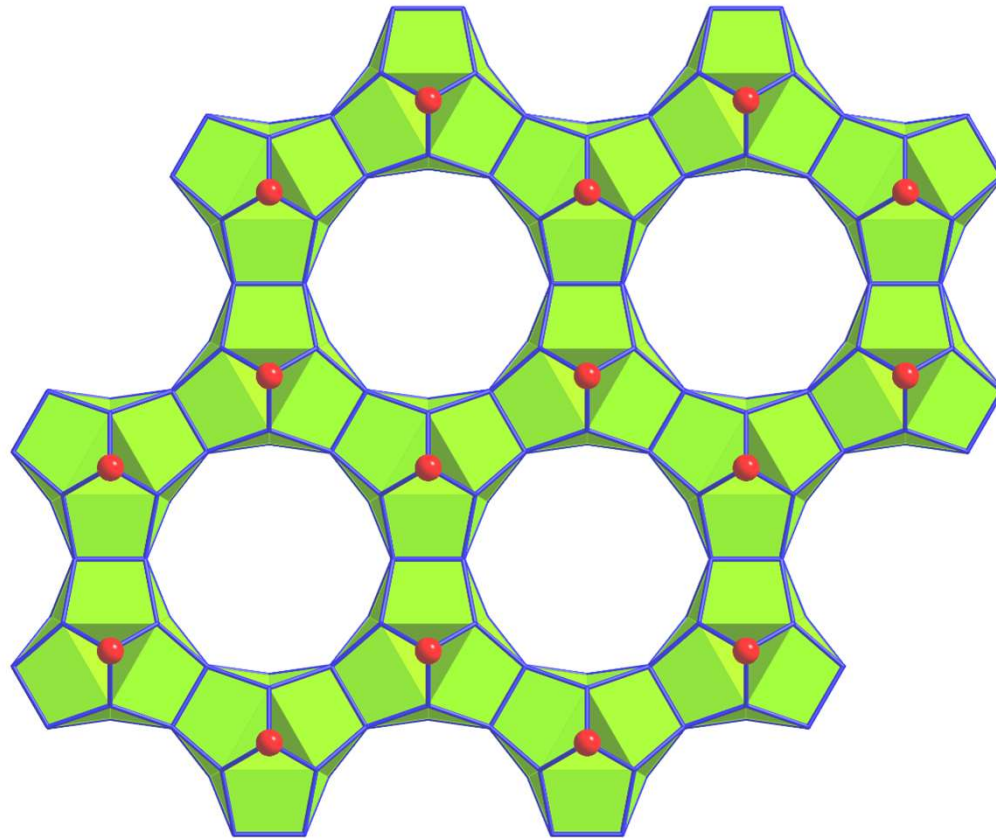
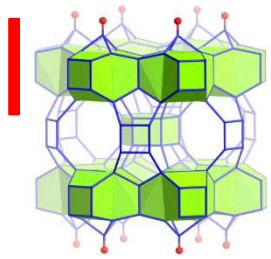


**SSZ-70**

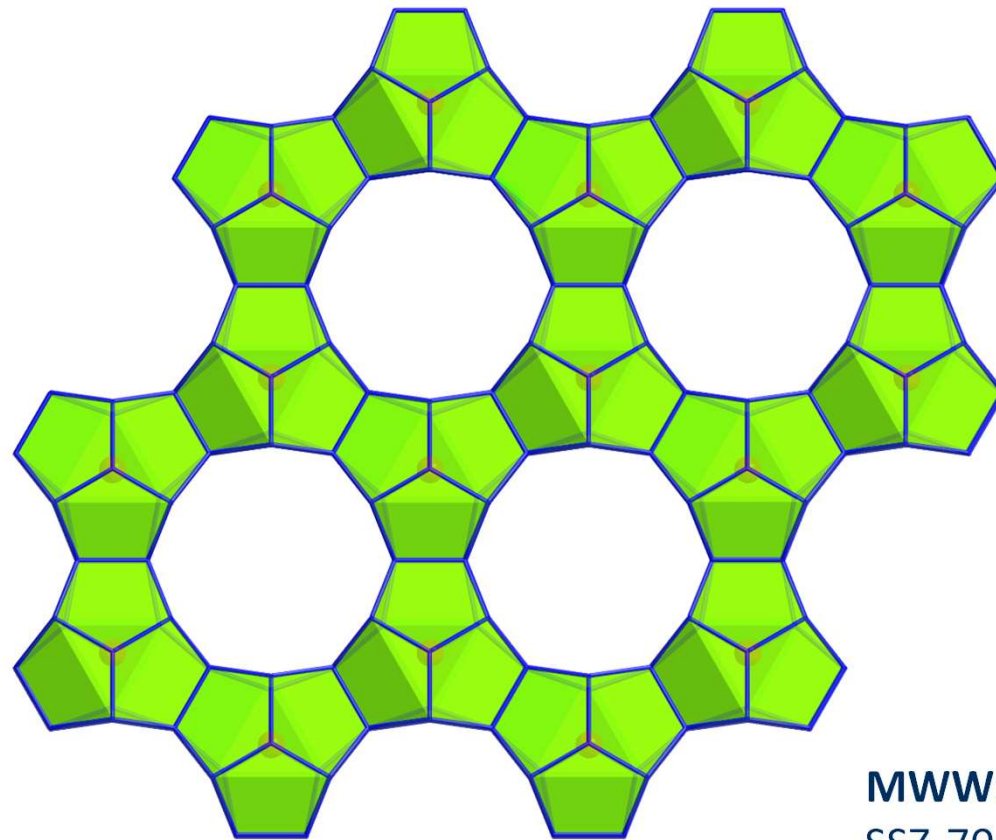
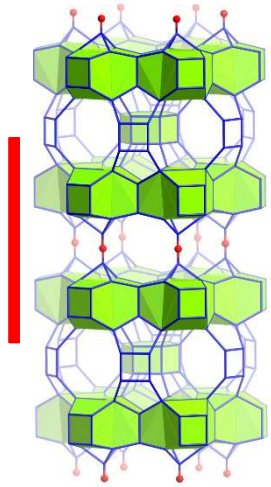
# Calcined SSZ-70



# Stacking



# Stacking AA

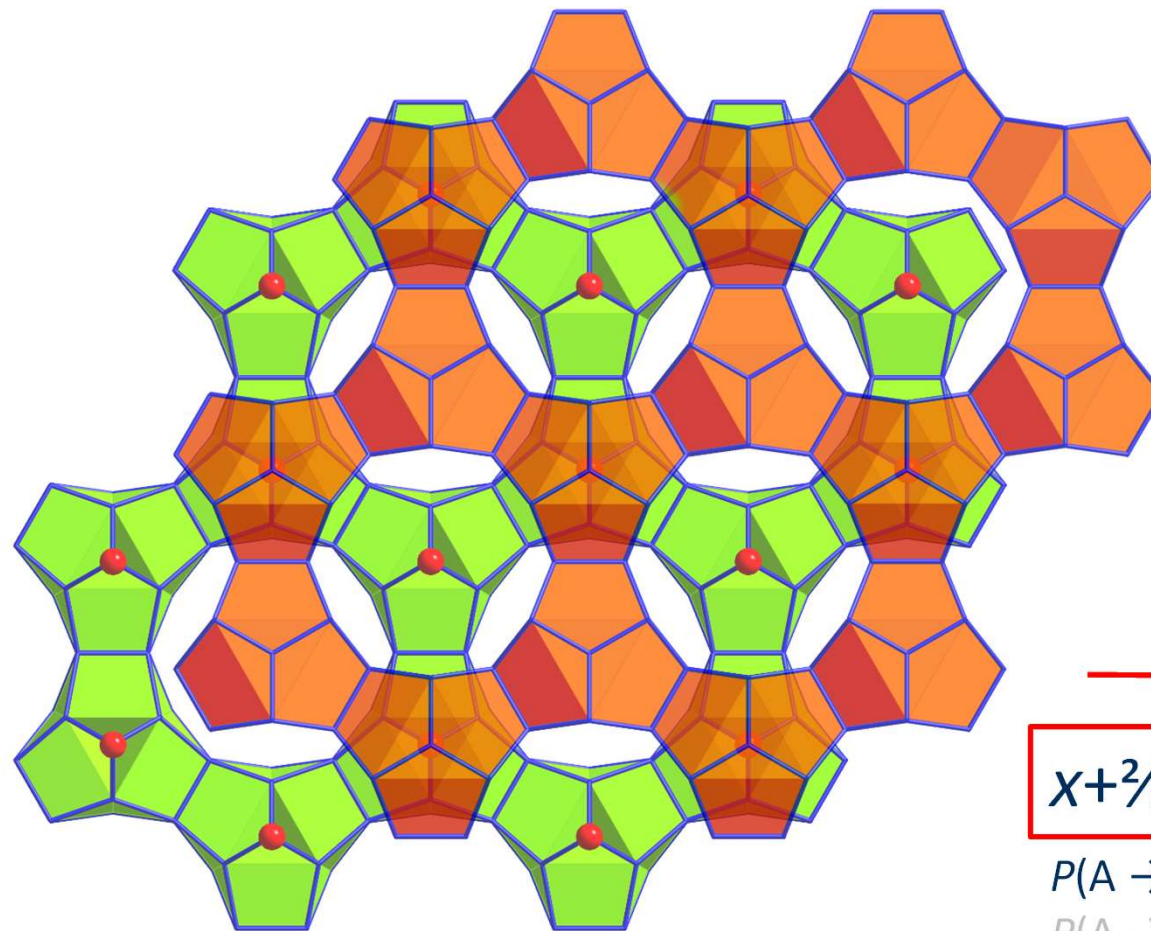
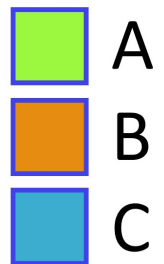
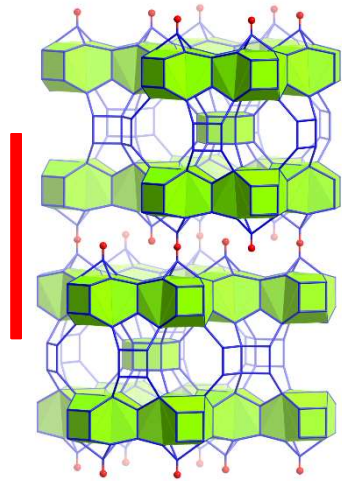


MWW:  $P(A \rightarrow A) = 100\%$

SSZ-70:  $P(A \rightarrow A) = 0\%$



# Stacking AB

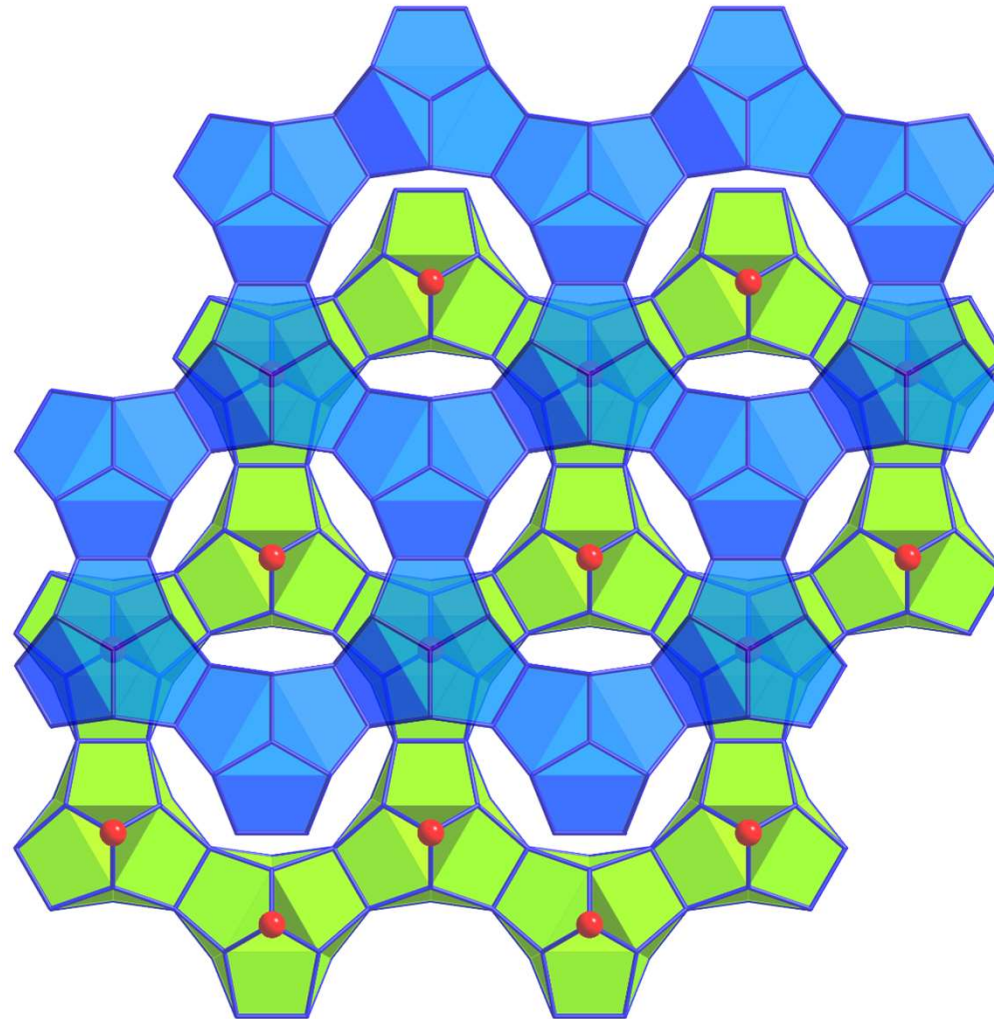
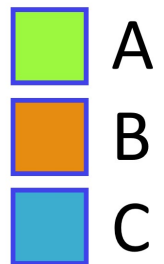
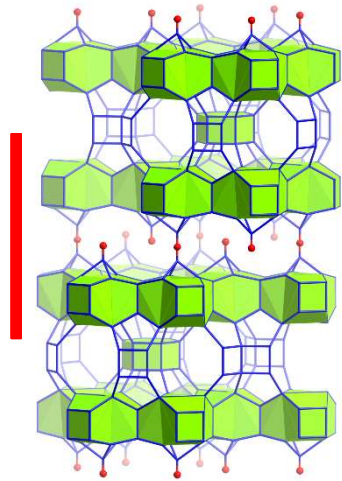


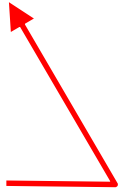
$$x+\frac{2}{3}, y+\frac{1}{3}$$

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

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

# Stacking AC

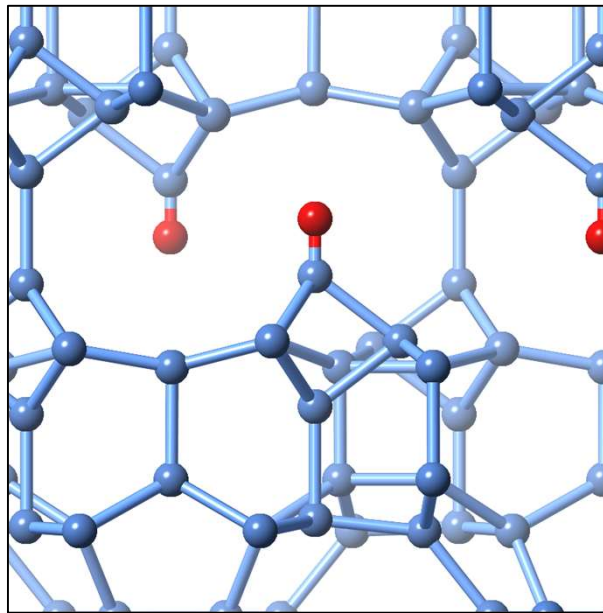



$$x+\frac{1}{3}, y+\frac{2}{3}$$

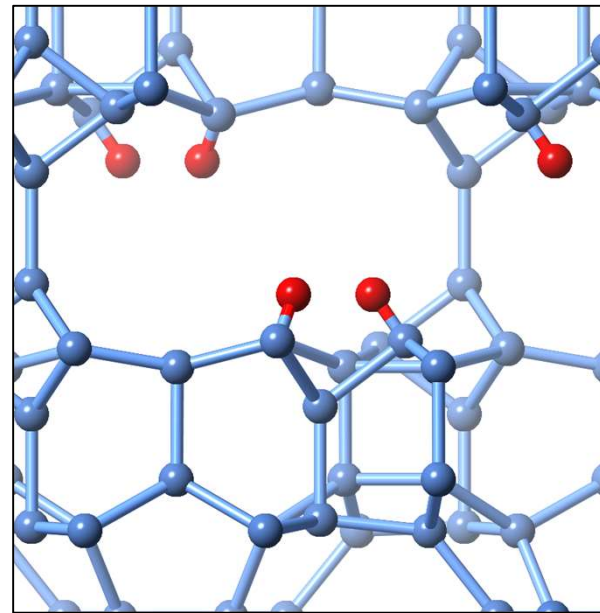
$$P(A \rightarrow B) = 50\%$$

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

# Interlayer region

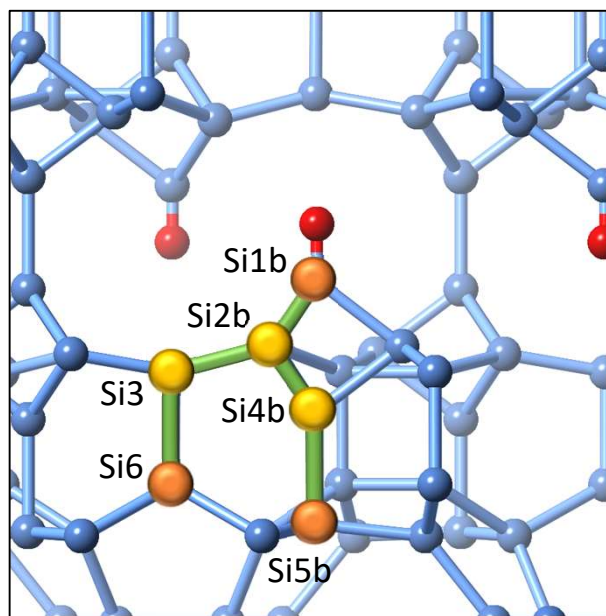


Model 1

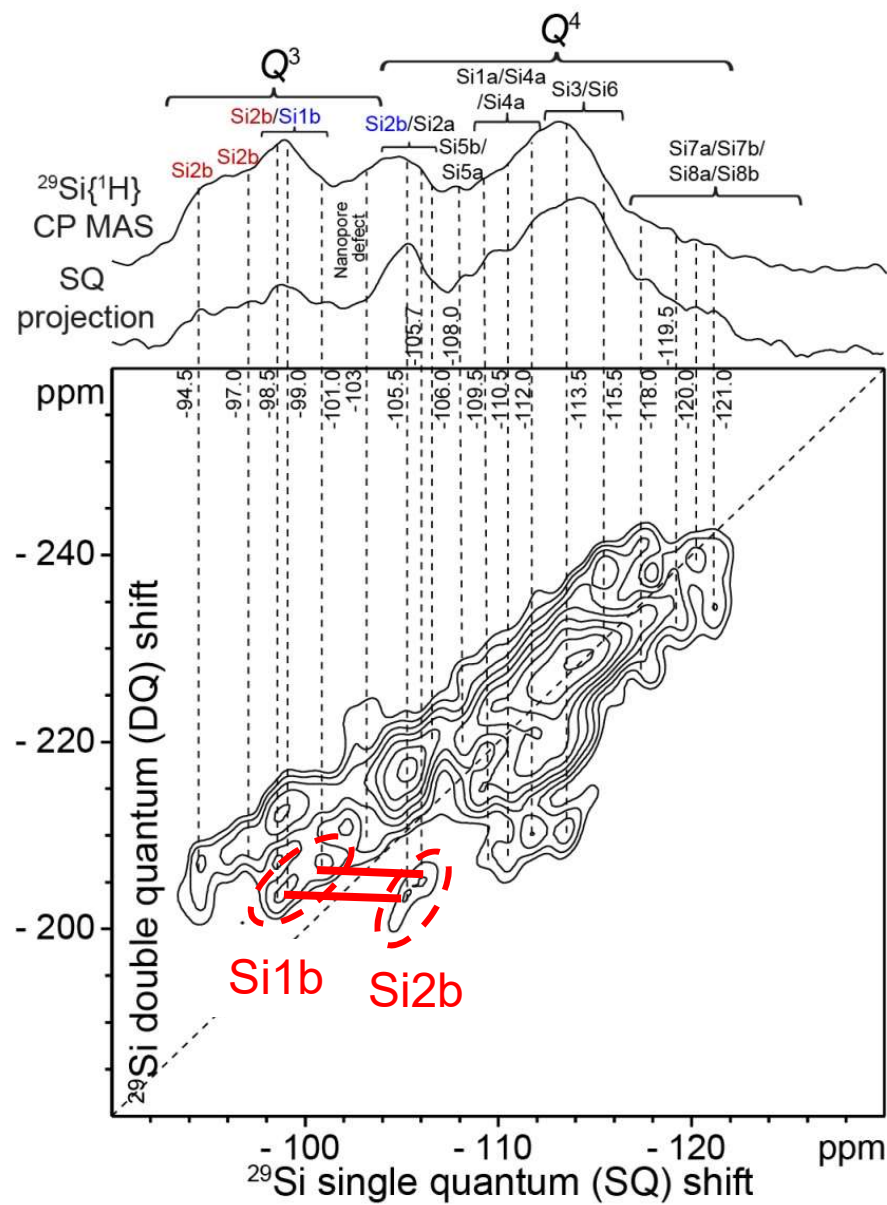


Model 2

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

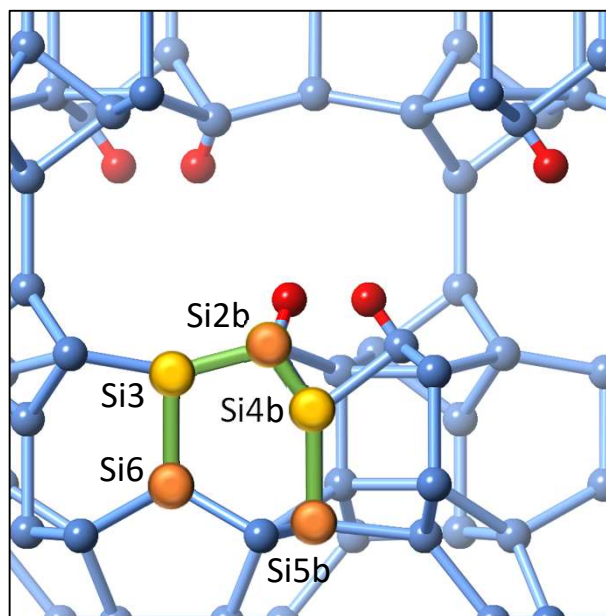


Model 1

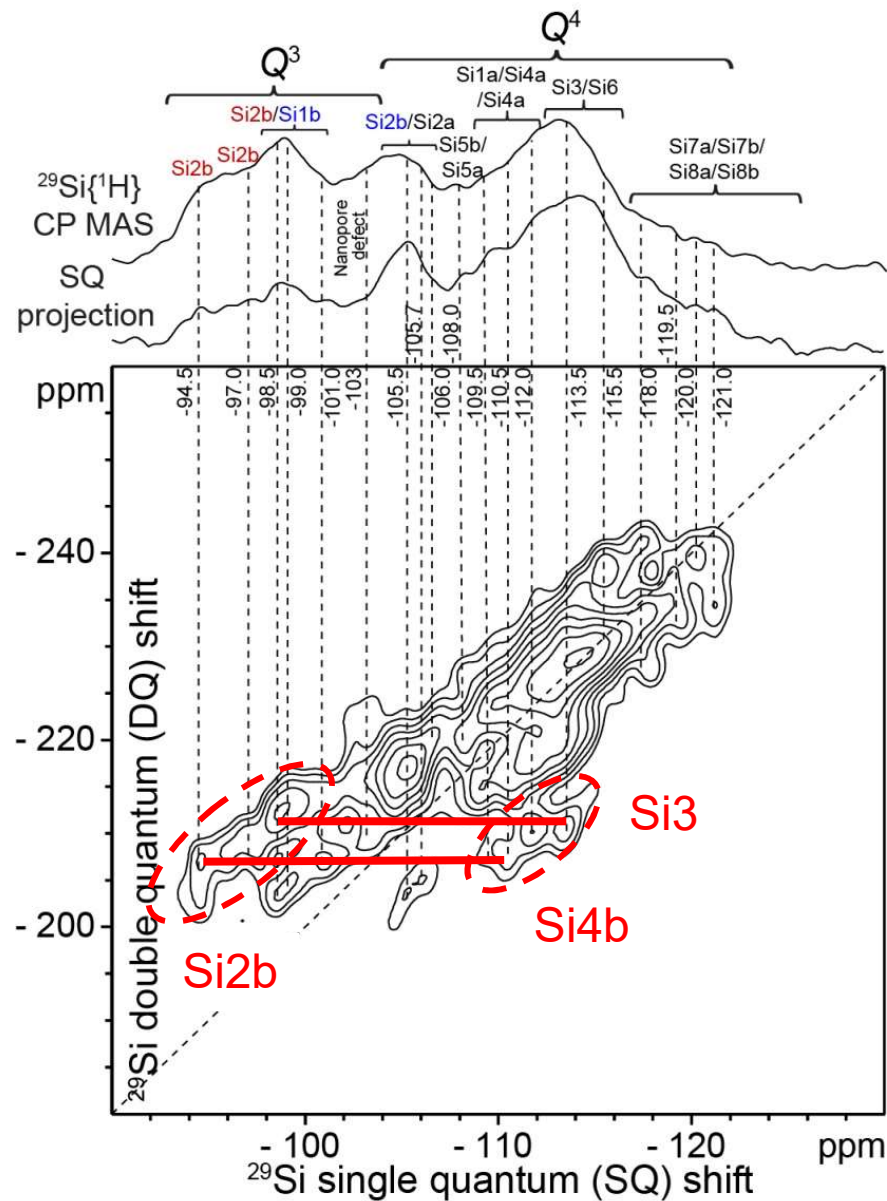




# 2D DNP-enhanced *J*-mediated NMR

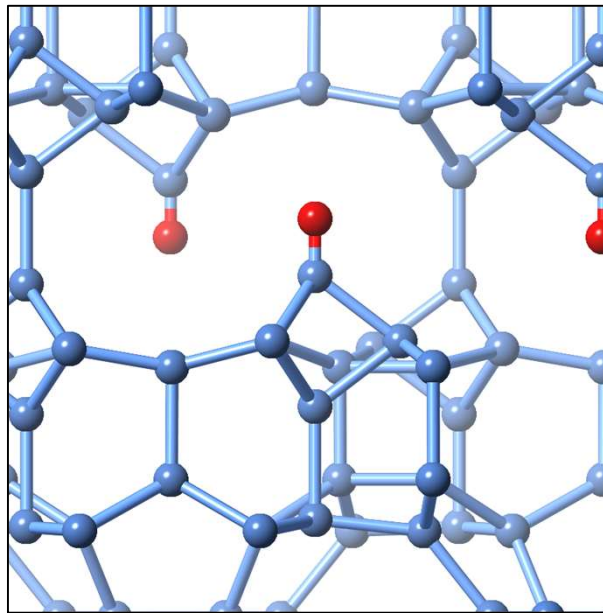


Model 2



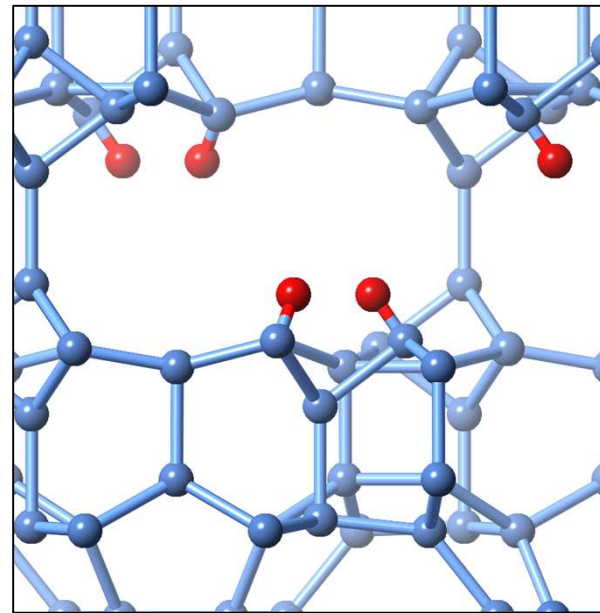


# Interlayer region



Model 1

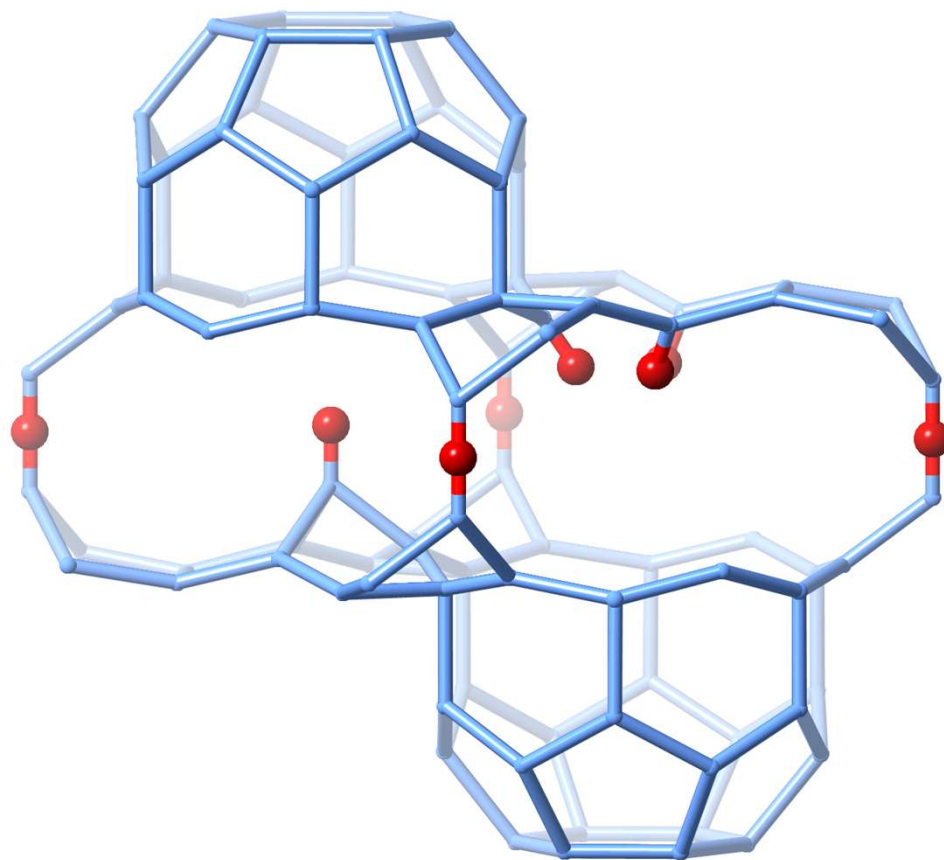
50%



Model 2

50%

## Structure of SSZ-70



# Conclusions

- Structure of SSZ-70 determined by combining methods
  - HRTEM → Disorder
  - XRPD → Average structure
  - DNP-enhanced 2D NMR → Nanostructure
- New stacking arrangement of **MWW**-layers

