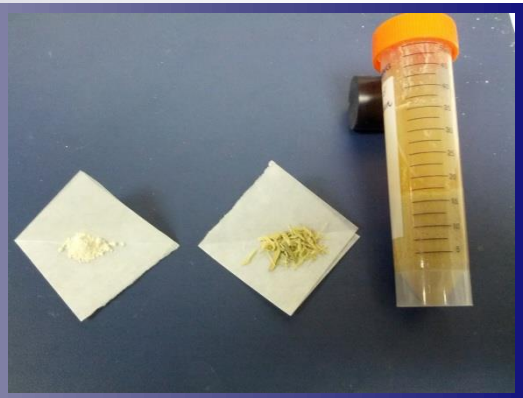
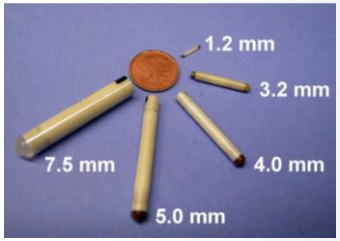
Solid State NMR Spectroscopy

by Andre Sutrisno

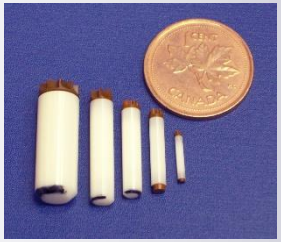
Solid State NMR
Why Solid State NMR?

- **Non-Destructive / “precious” samples**
- **Additional information not available from solution NMR**
- **Solid/Semi-solid samples / Insoluble / No solvent needed**
- **Native states = “as is” - no treatment, approach**

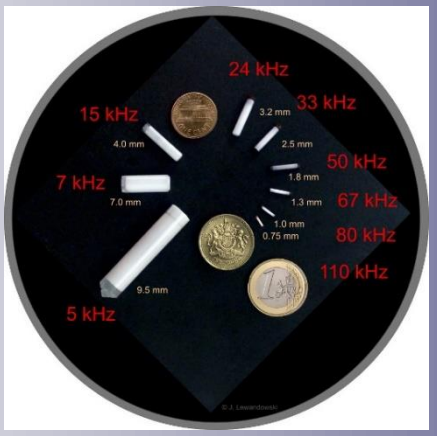


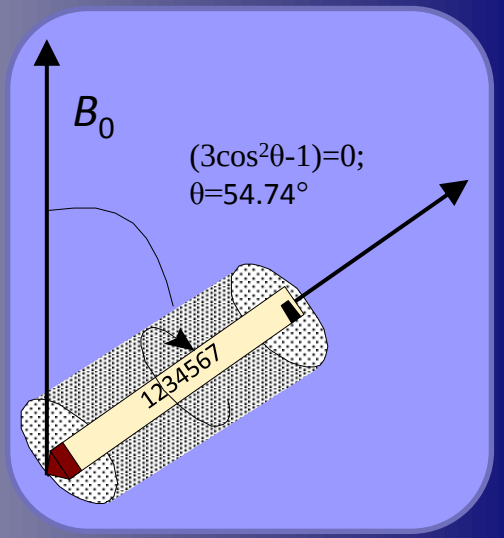


Varian/Agilent NMR rotors



Bruker NMR rotors





Solid State NMR Spectroscopy

Solid State NMR

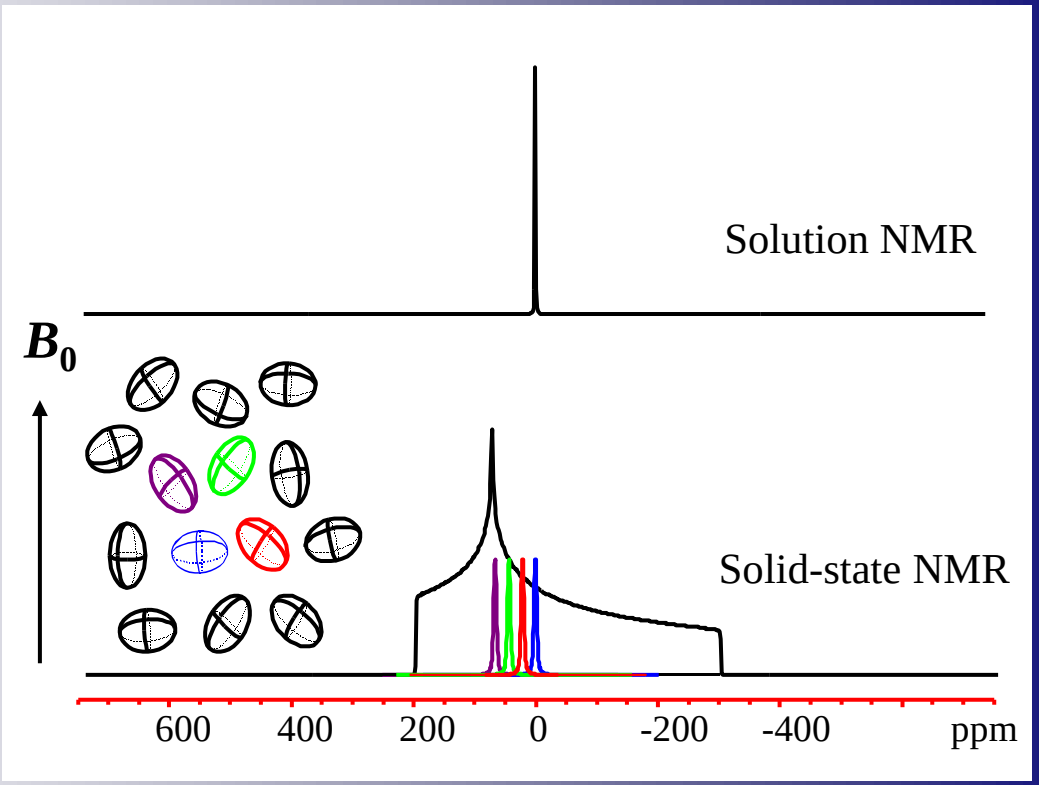
Differences from Solution-State

Solution NMR:

- **sharp, well resolved peaks**
- **molecular tumbling**
- **averages out the NMR interactions**

Solid state NMR:

- **broad powder patterns**
- **reduce both resolution and sensitivity**



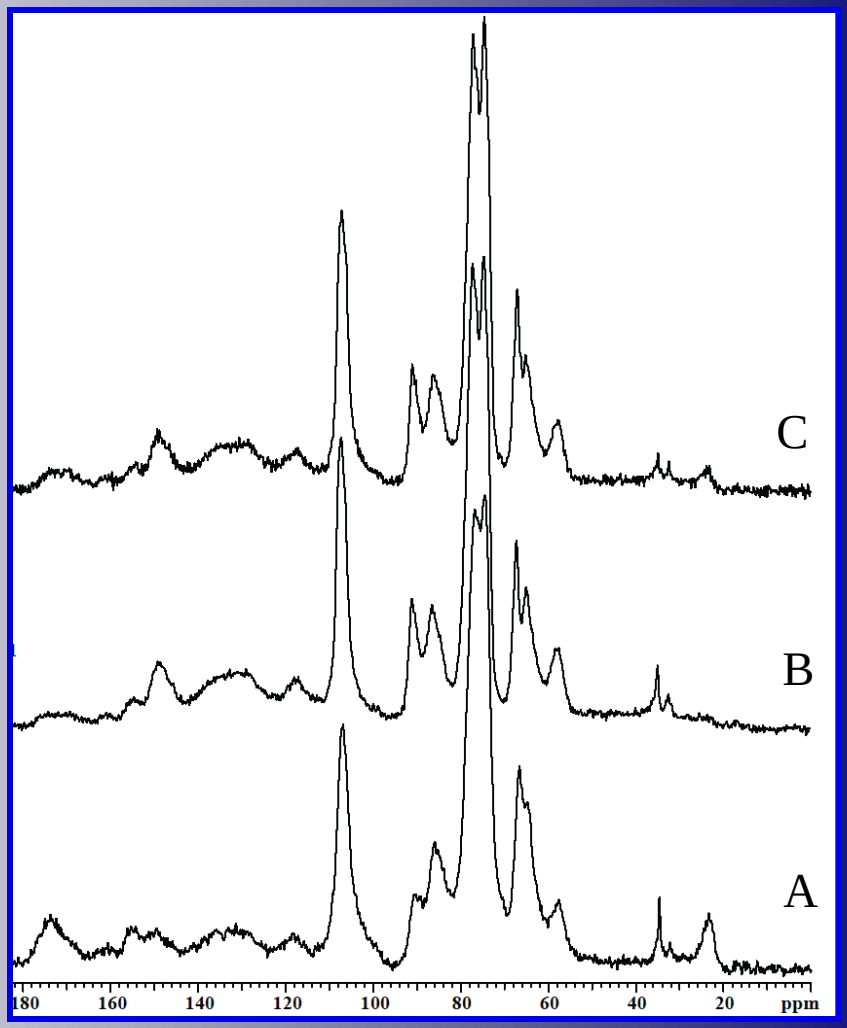
- **Need to create solution-like motion and narrow line widths**
  - **Magic Angle Spinning (MAS)**
  - **High power (kW) ^{1}H decoupling**

^{13}C CPMAS NMR Depicts Degree of Crystallinity

Solid State NMR Research Examples

- **CPMAS = Cross-Polarization MAS**
  Able to transfer magnetization from nuclei with high natural abundance to those with low natural abundance for signal enhancement due to dipolar interactions

- **Measure *line width***
  - **narrower line width (sharper the peak), more crystalline**
- **Measure *relaxation parameters*, $T_{1\rho}$ (spin-lattice relaxation time)**
  - **the longer $T_{1\rho}$, the more crystalline**



Ability to Follow Slow Reaction Processes (Kinetics)

Follow the transformation of "enol" to "keto" that occurs at room temp

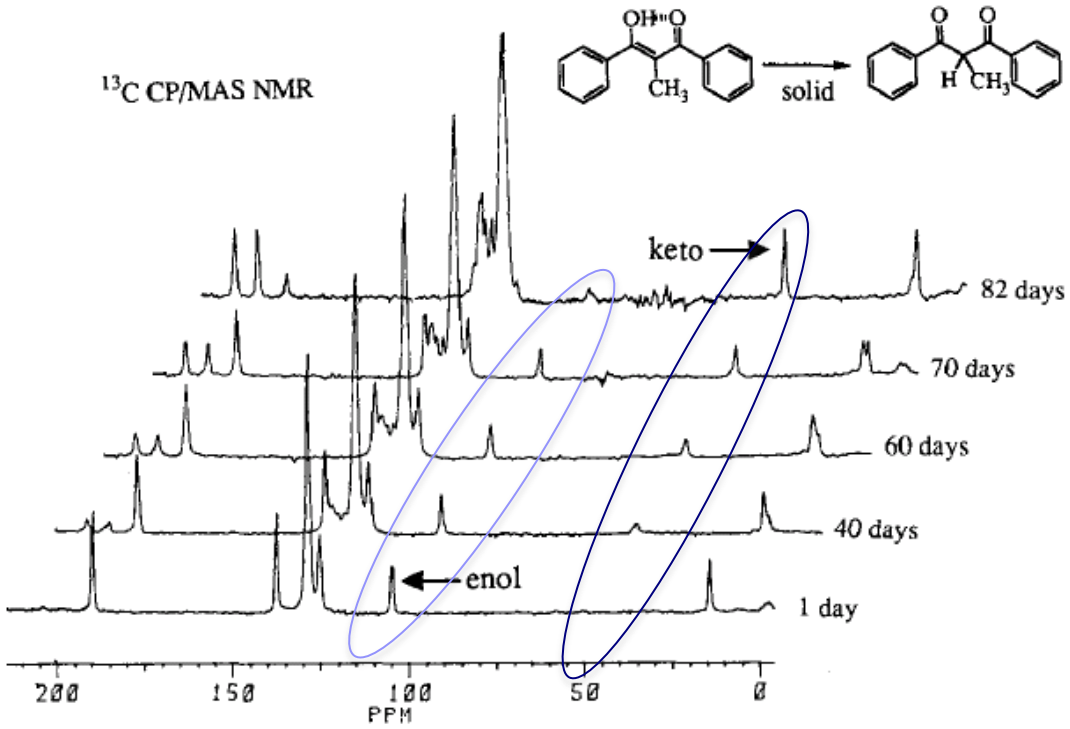
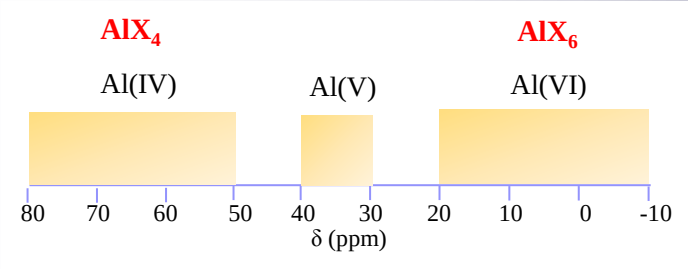


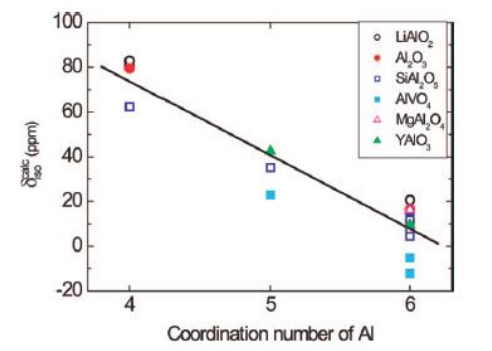
Fig. 8. A series of ^{13}C CP/MAS NMR spectra which follows the solid-state reaction of $\mathbf{IV}_{enol} \rightarrow \mathbf{IV}_{keto}$. The transformation occurs at room temperature and is easily monitored by NMR.

NMR Chemical Shifts and Coordination

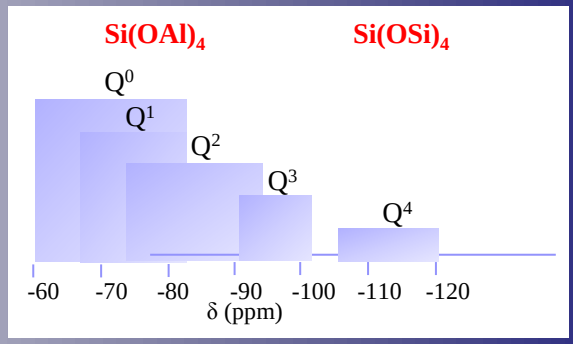
Well-established chemical shift ranges for different species

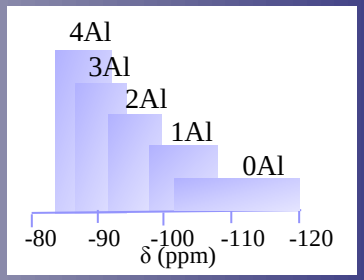
^{27}Al





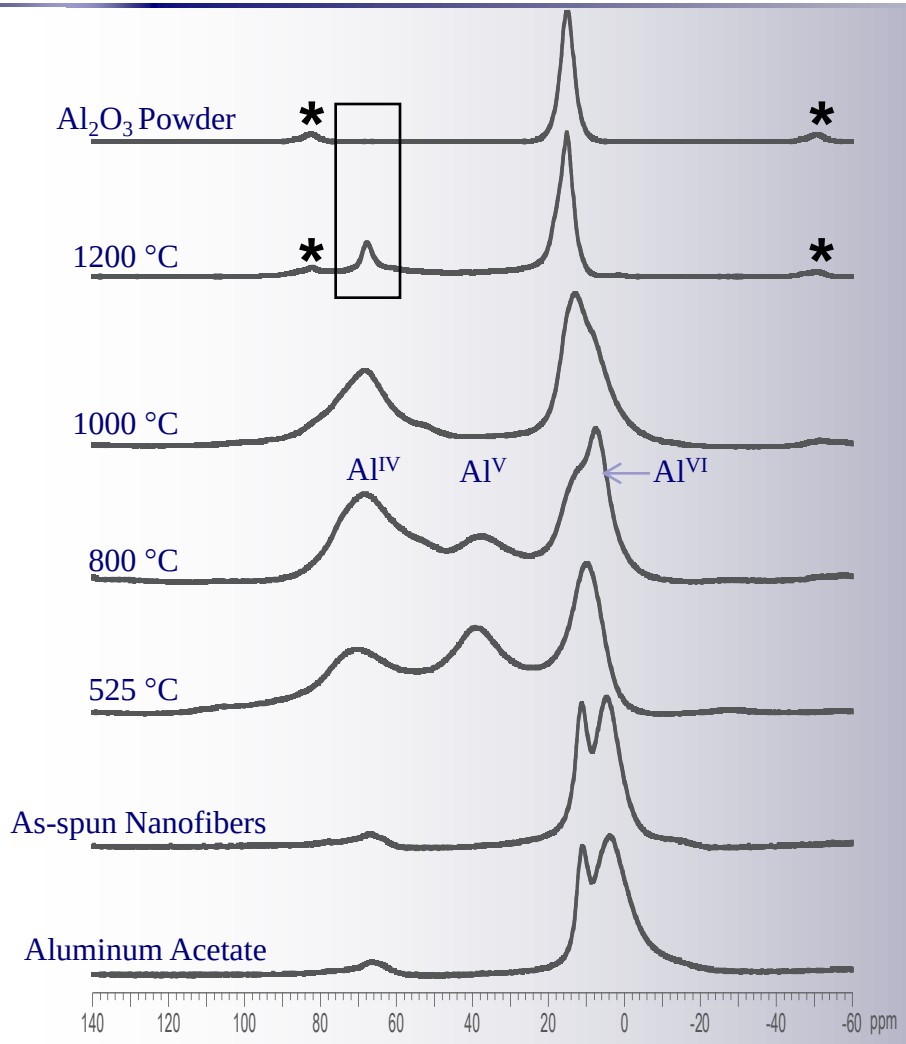
^{29}Si

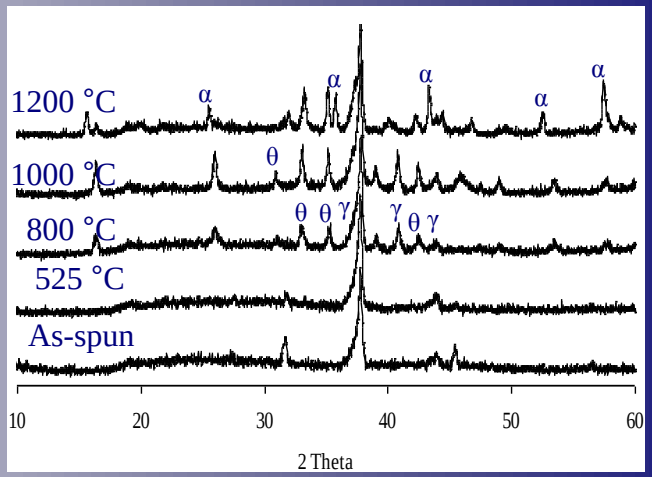




^{27}Al MAS NMR Depicts Various Transition Phases from Thermal Treatment

Solid State NMR Research Examples





Boehmite: $\gamma \rightarrow \delta \rightarrow \theta + \alpha \rightarrow \alpha$

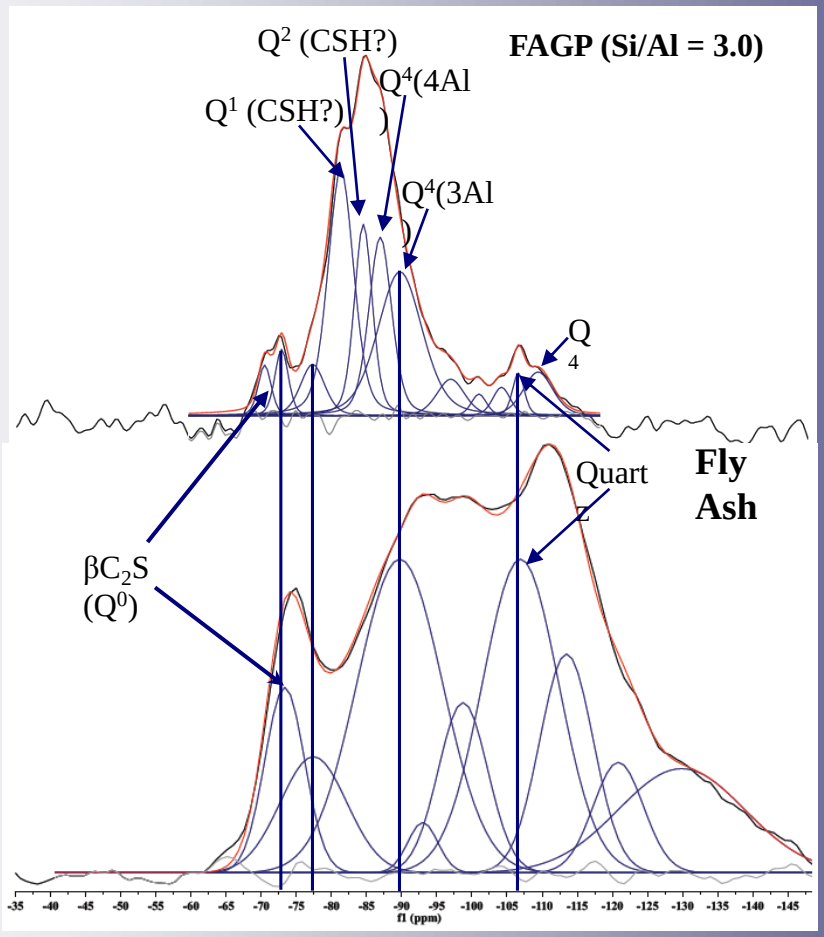
XRD is an excellent complementary technique

De-convolution of ^{29}Si MAS peaks provides structural information and degree of reactivity

Solid State NMR Research Examples

^{29}Si 1D SSNMR spectra of fly ash geopolymers before and after reaction

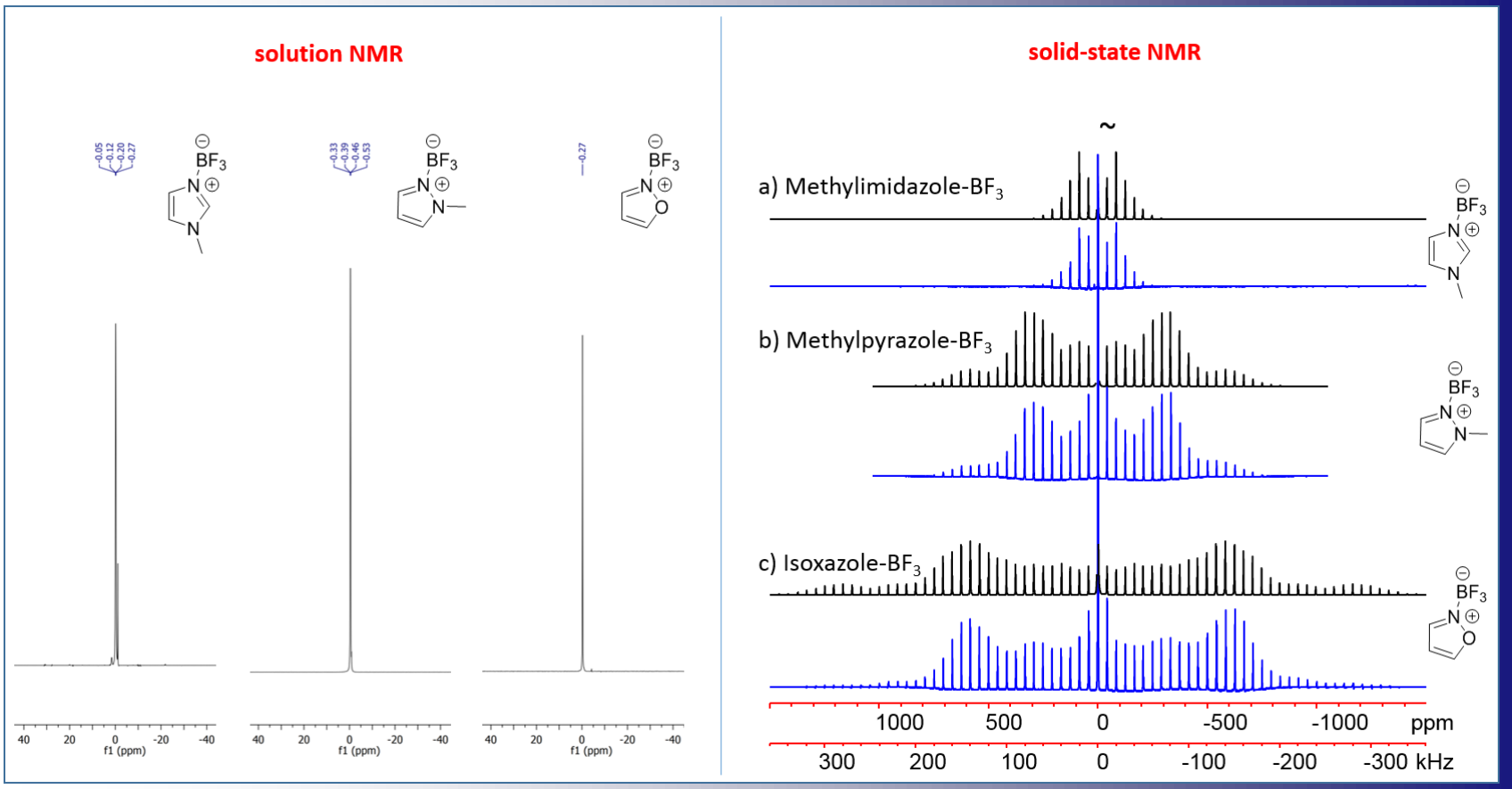
- Beginning to identify structural components via deconvolution of the peaks
- Ratio between different Q sites change



1D ^{11}B MAS spectra are very sensitive to detect changes in local environment around B atoms

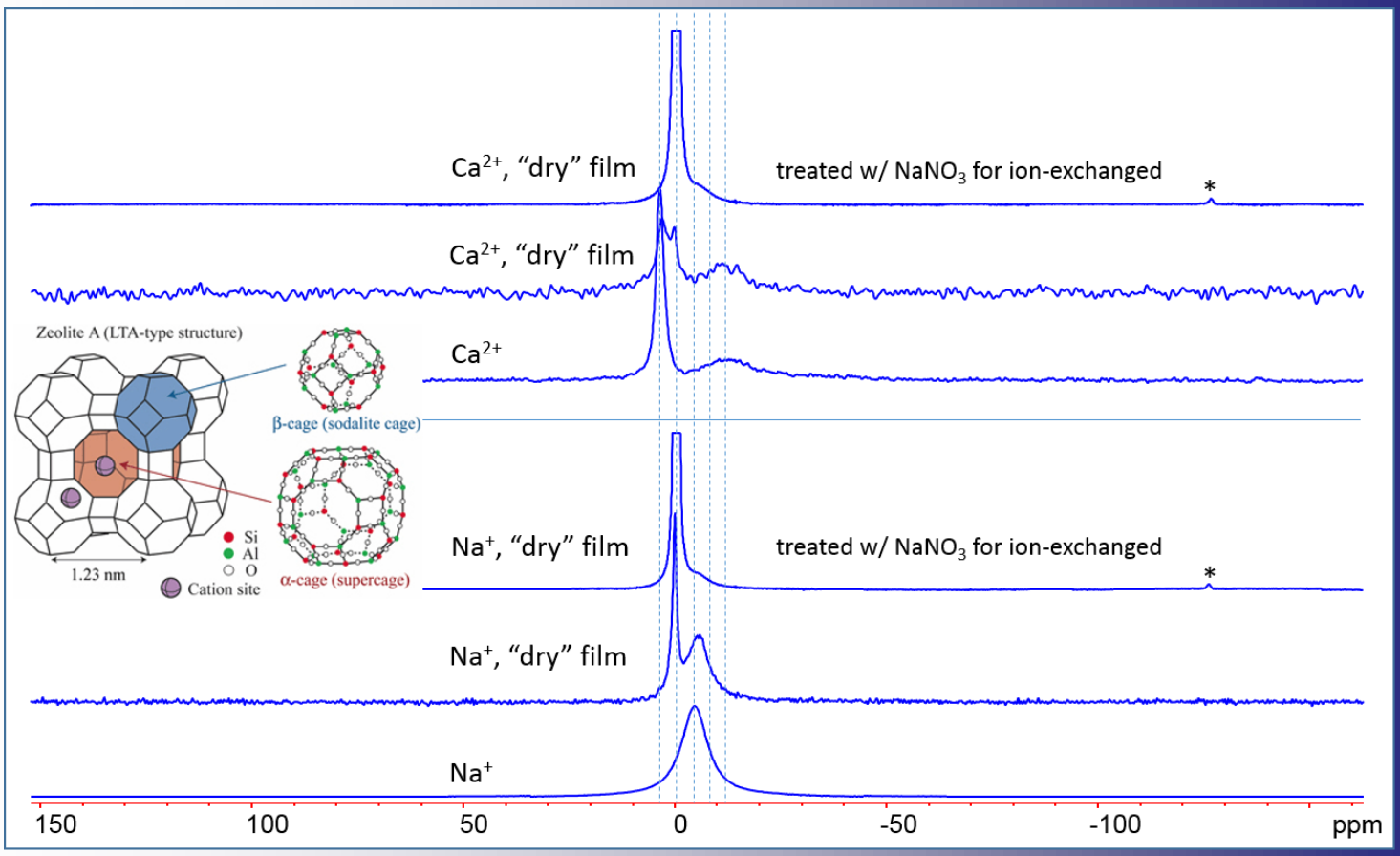
Solid State NMR Research Examples

^{11}B EFG tensors serve as a powerful probe to detect subtle changes in the electronic nature of the studied structures



^{23}Na MAS spectra of zeolite A powder inside PAA polymer film

Na^+ - more symmetric vs. Ca^{2+} - "line shape"; native state vs. inside film



^{119}Sn and ^{65}Cu MAS spectra of CZTS semiconductors

Solid State NMR Research Examples

Shows evidence of the presence of two different phases as a mixture