Joint Laboratory of Solid-State NMR
IMC AS CZ and JHPC AS CZ

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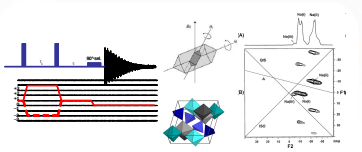
(4)

Structural characterization of inorganic aluminosilicate systems: role of water

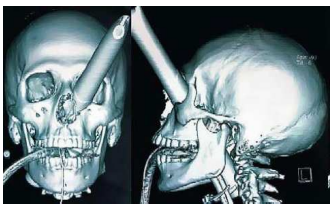


Outlook

- **Introduction - ss-NMR of inorganic systems**
  - NMR crystallography
  - Problem of quadrupolar nuclei
  - Removing of quadrupolar broadening (DOR, MQ/MAS)
  - Enhancement of spectral resolution
- **Structure of aluminosilicate systems**
  - Amorphous aluminosilicate inorganic polymers (AIP) - synthesis
  - Primary structural data about Al/Si materials - ^{29}Si a ^{27}Al MAS NMR
  - Amorphous-crystalline phase transition of AIPs
  - How to get structural parameters
    - ^{29}Si, ^{27}Al, ^{23}Na MAS NMR
    - ^{27}Al MQ/MAS NMR
    - ^{1}H MAS NMR and spin relaxation
    - ^{29}Si CP/MAS a REDOR NMR (*localization of H_2O*)
    - VA-CT ^{29}Si CP/MAS (*hydration extent*)
    - ^{1}H-^{1}H MAS (*interaction network*)
    - ^{27}Al REDOR MQ/MAS NMR
    - Structural model

Is NMR spectroscopy really such unique method?

Magnetic Resonance Imaging



Concept of NMR crystallography

NMR crystallography

X-ray (Powder) Diffraction
- diffraction pattern
- pair distribution function analysis
- etc.

Molecular Modeling
- conformation (DFT)
- prediction of long-range arrangement
- NMR parameters (CASTEP)
- etc.

structural fragments

process of structure refinement

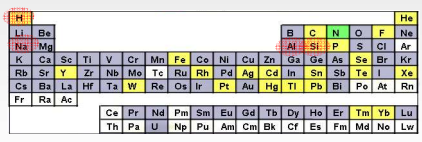
Refined structure with incorporated segmental dynamics, intermolecular interaction and supramolecular architecture

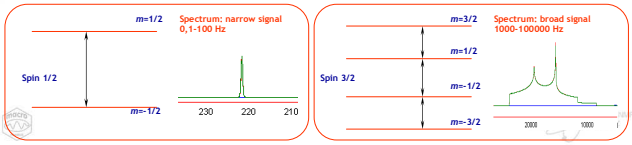
ss-NMR Spectroscopy
- ^{1}H-^{1}H spin-exchange
- ^{1}H-^{13}C contacts
- ^{1}H-^{15}N distances
- motional frequencies
- motional amplitudes
- chemical shifts
- etc.

Applications
- Finding relations between molecular structure, and physicochemical properties (bioavailability) of...
- ... pharmaceuticals based on solid solution and solid dispersions of API in polymer matrix,

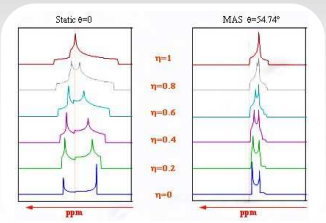
NMR active nuclei - problem of inorganic systems; *I*>1/2

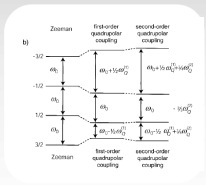
22 spins *I*=1/2
77 spins *I*=3/2, 5/2, 9/2
1 spin *I*=1





Quadrupolar broadening

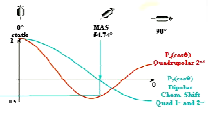




$$P_2(\cos\theta) = \frac{1}{2}(3\cos^2\theta - 1) = 0$$

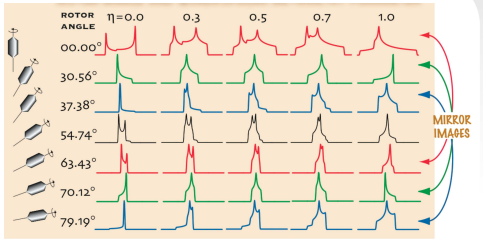
$$P_4(\cos\theta) = \frac{1}{8}(35\cos^4\theta - 30\cos^2\theta + 3) = -7/18$$

$\theta = 54.74°$



MAS narrows 2nd order broadening only by a factor 3 to 4

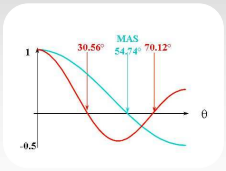
Quadrupolar broadening and MAS (off-MAS)



$$P_2(\cos\theta)=\frac{1}{2}\left(3\cos^2\theta-1\right)$$

$$P_4(\cos\theta)=\frac{1}{8}\left(35\cos^4\theta-30\cos^2\theta+3\right)$$

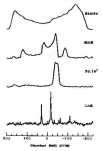
DAS: Dynamic Angle Spinning

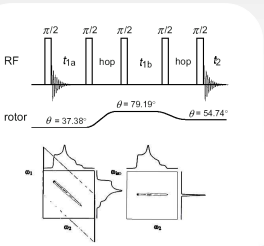


$$P_2(\cos\theta)=\frac{1}{2}\left(3\cos^2\theta-1\right)$$

$$P_4(\cos\theta)=\frac{1}{8}\left(35\cos^4\theta-30\cos^2\theta+3\right)$$

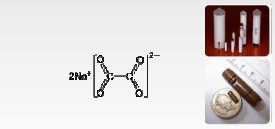
^{17}O DAS crystobalit

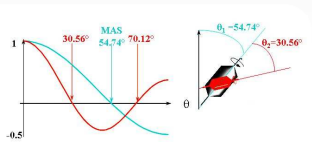


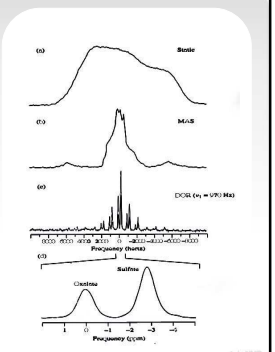


DOR: Double Rotation

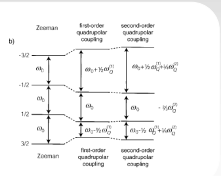
^{23}Na DOR of sodium oxalate

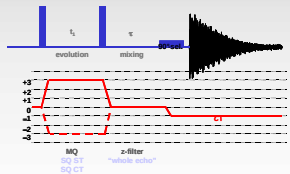


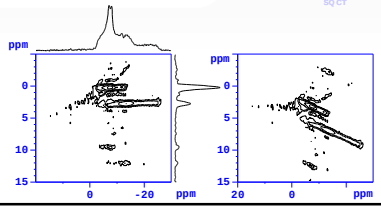




Multiple-quantum NMR spectroscopy





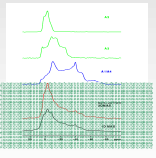


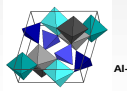
^{23}Na MQ/MAS $Na_2HPO_4.H_2O$

Multiple-quantum NMR spectroscopy

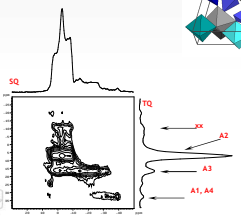
^{27}Al 3Q MAS of Kyanite at different fields

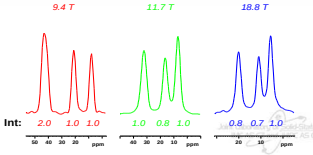
- Kyanite, z-filtered experiment at 11.7 T
- anisotropic traces
- traces for A1 and A4 cannot be resolved
- 27 kHz MAS frequency
- 250 kHz RF
- excitation pulse: 1.9 µs
- conversion pulse: 0.7 µs
- 90° selective pulse: 11 µs





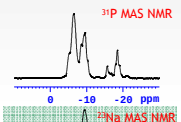
Al-27 3Q MAS traces of Kyanite at different fields

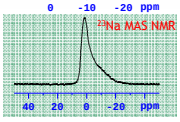


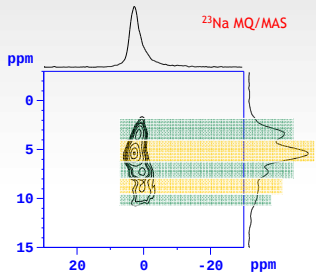


MQ/MAS NMR spectroscopy - polymorphism of ATP

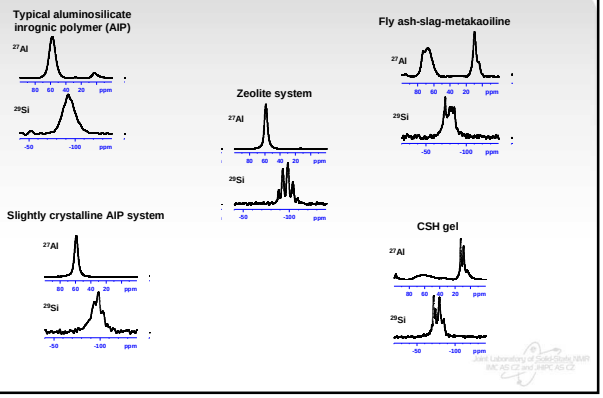
Form III



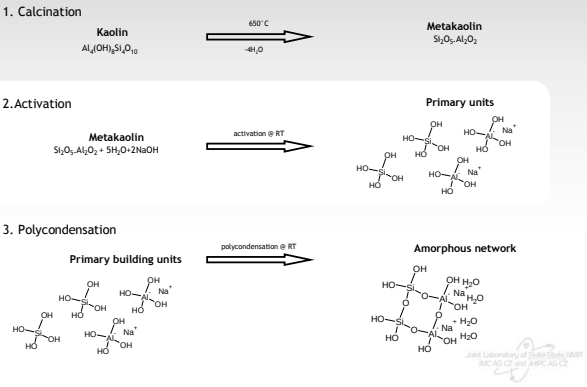




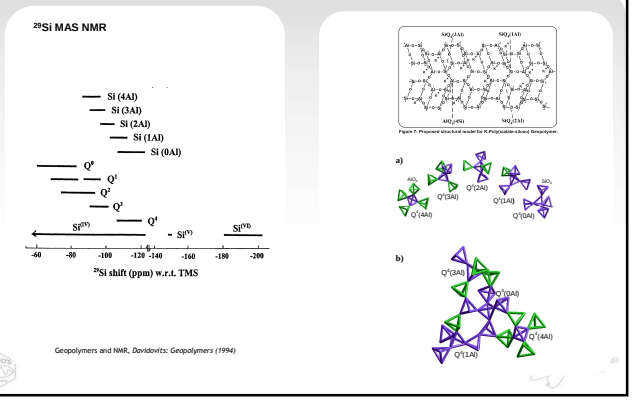
Variability of Al/Si materials



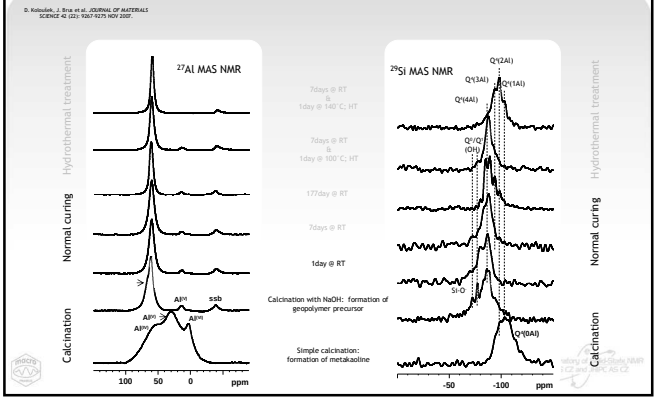
Synthesis of AIP systems



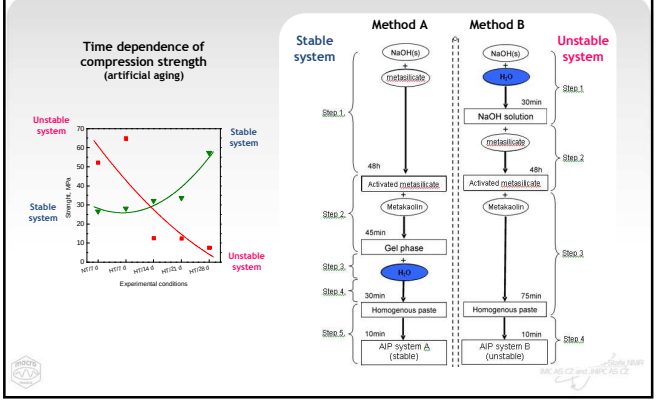
Structure of AIP systems



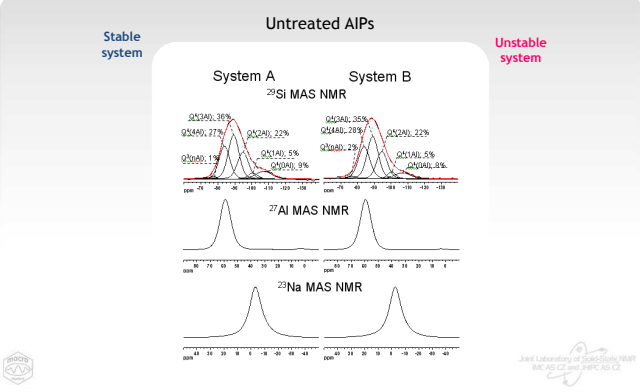
Synthesis of AIP systems



Structural instability of AIPs: spontaneous crystallization



Basis structural parameters: ^{29}Si,^{27}Al,^{23}Na MAS NMR



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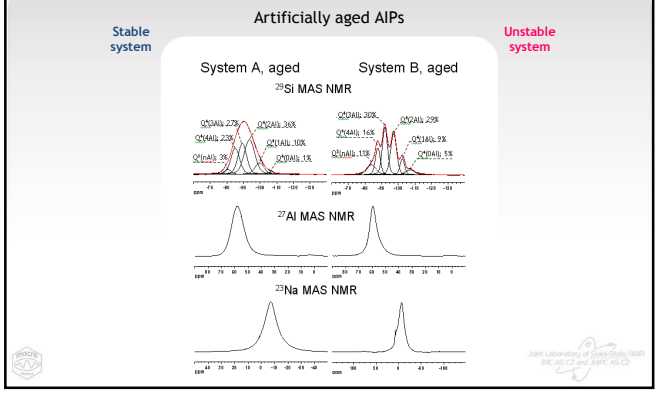
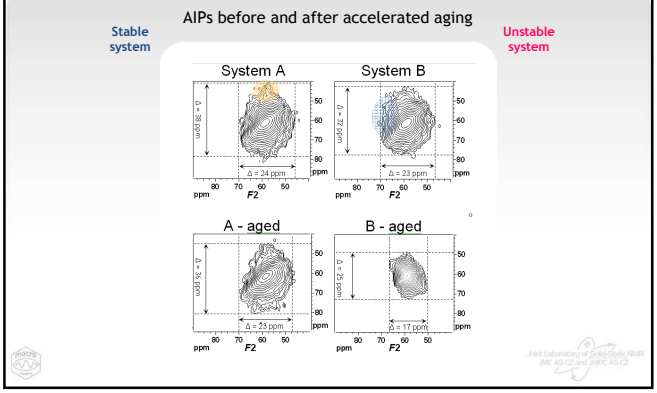
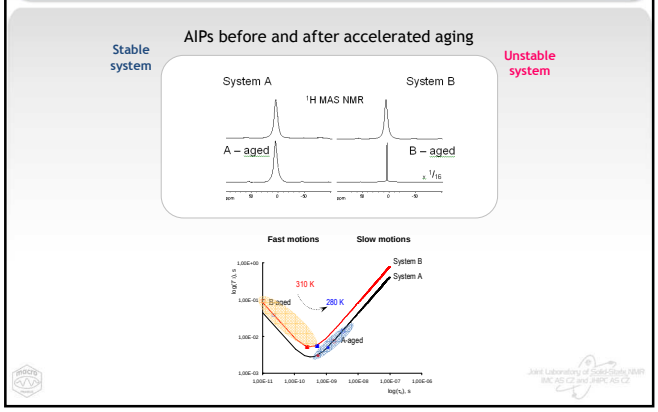


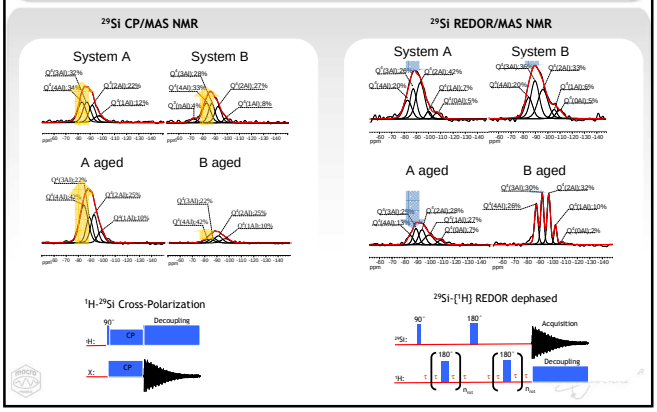
Basis structural parameters: ^{27}Al MQ/MAS NMR



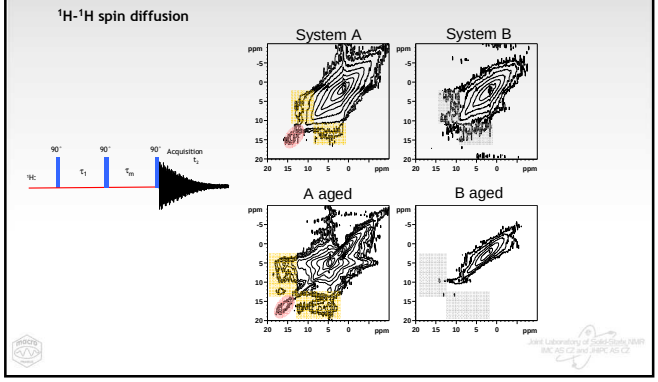
Basis structural parameters : ^{1}H MAS NMR, relaxation



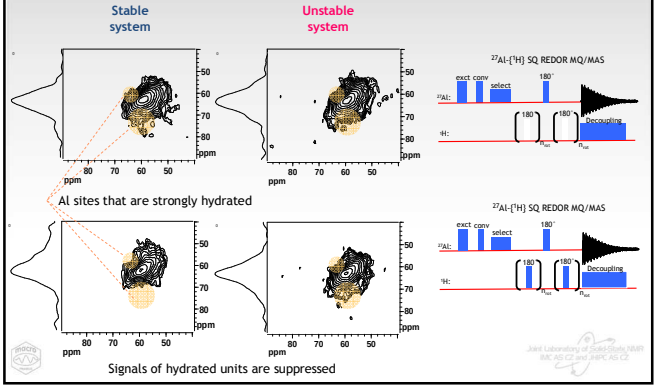
Hydration of star clusters Q^4(*n*Al)



Hydrogen-bonding network: H_2O/-OH/H^+



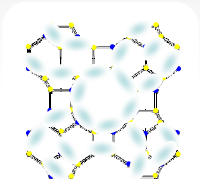
Hydration of Al sites: ^{27}Al {^{1}H}-REDOR MQ/MAS NMR

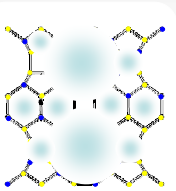


Structural model of stable and unstable AlPs

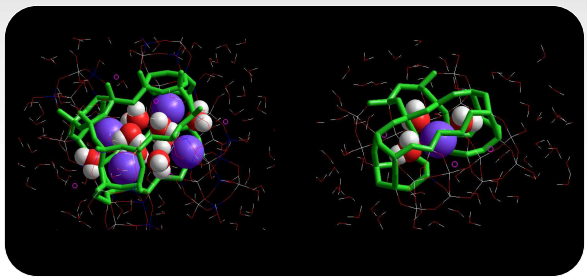
$$\delta cs(ppm) = \frac{10}{27}\delta_t + \frac{17}{27}\delta_{oo} \quad (\delta cs - \text{chemical shift})$$

	T–O–T angle(°)	T–T distance(A)
Stable system		
$\delta cs_1(M) = 65.02ppm$	133	3.03
$\delta cs_1(U) = 67.16ppm$	131	< 3
$\delta cs_2(M) = 63.76ppm$	137	3.05
$\delta cs_2(U) = 61.44ppm$	143	3.12
$\delta cs_3(M) = 57.39ppm$	148	3.16
$\delta cs_3(U) =$	no differences	
Unstable system		
$\delta cs_4(M) = 70.06ppm$	125	< 3
$\delta cs_4(U) =$	no differences	





Structural model of stable AlPs



Summary