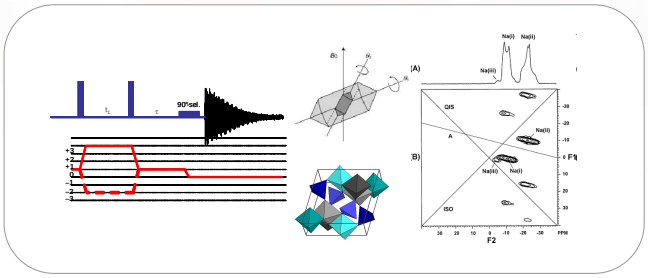
Joint Laboratory of Solid-State NMR
IMC AS CZ and JHIPC AS CZ

Institute of Macromolecular
Chemistry AS CR
Heyrovský Sqr. 2
162 06 Praha 6
Czech Republ.

(11)
jiri brus

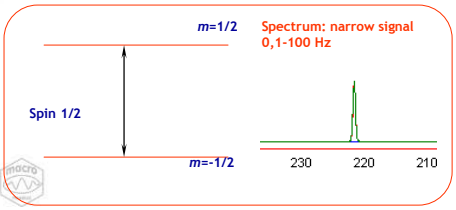
Problém kvadrupolové interakce

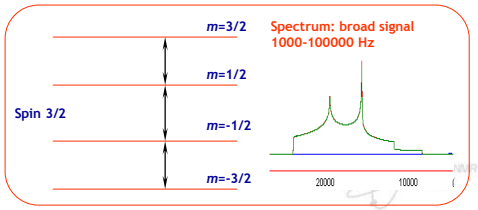


NMR aktivní jádra

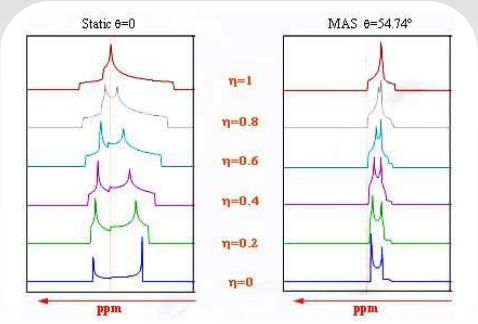
22 spins *I*=1/2
77 spins *I*=3/2, 5/2,9/2
1 spin *I*=1

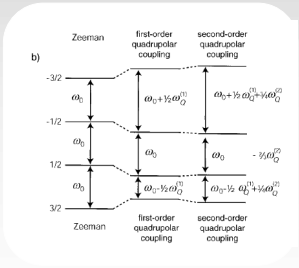
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw	

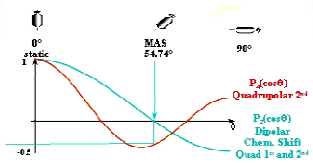




Kvadrupolové štěpení signálů







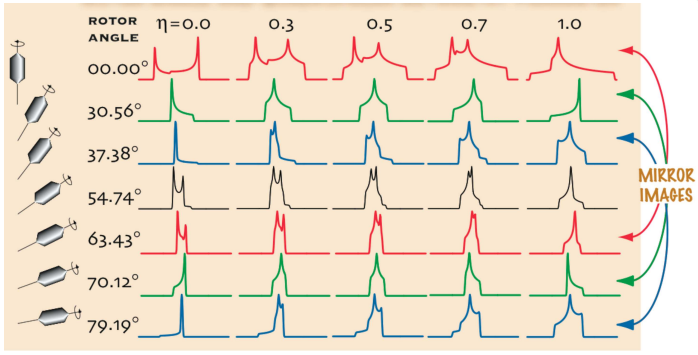
$$P_2(\cos\theta)=\frac{1}{2}\left(3\cos^2\theta-1\right) \qquad =0$$

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

$$\theta = 54.74°$$

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

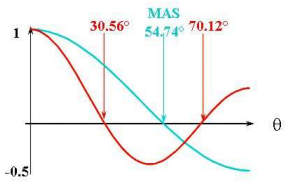
Kvadrupolové štěpení a rotace vzorku



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

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

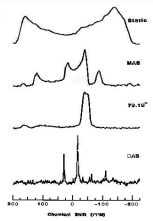
DAS: Dynamic Angle Spinning

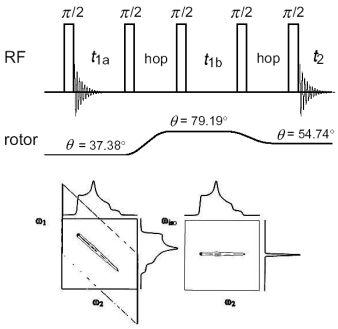


$$P_2(\cos\theta)=\frac{1}{2}\left(3\cos^2\theta-1\right)$$

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

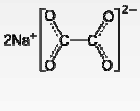
^{17}O DAS crystobalit

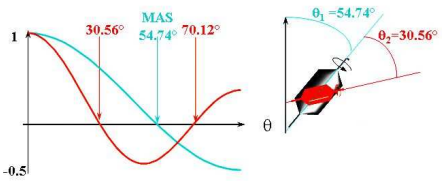


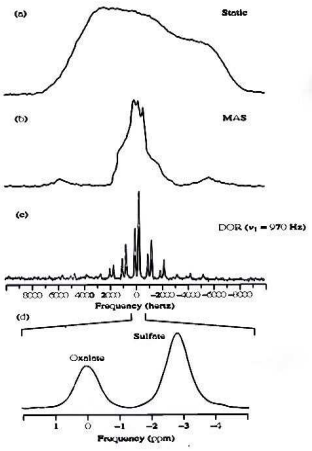


DOR: Dvojitá Rotace

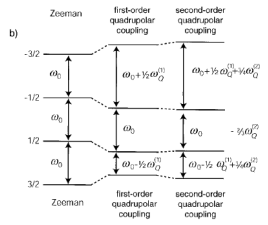
^{23}Na DOR of šťavelan sodný

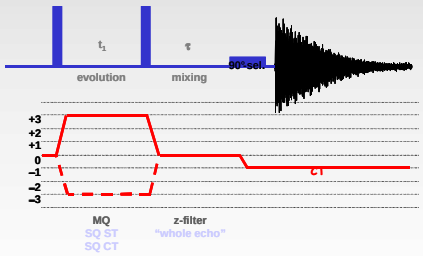


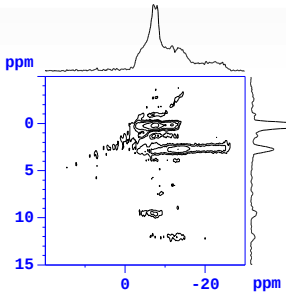


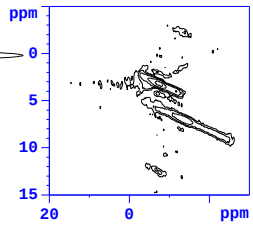


Vícekvantová NMR spektroskopie



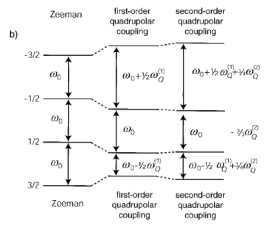


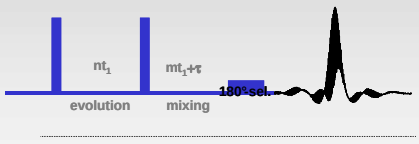


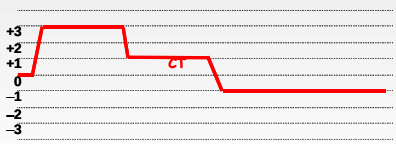


^{23}Na MQ/MAS $Na_2HPO_4.H_2O$

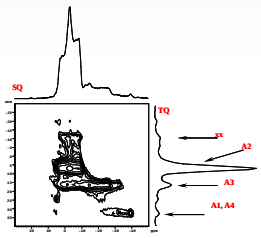
Vícekvantová NMR spektroskopie



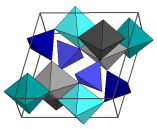




MQ
SQ ST
SQ CT
z-filter
"whole echo"

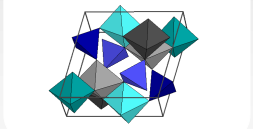


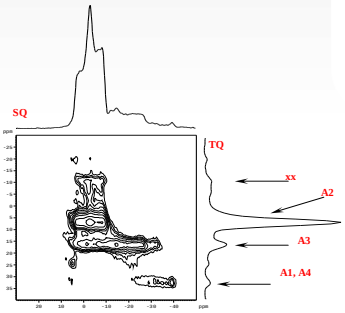
^{27}Al MQ/MAS kyanit

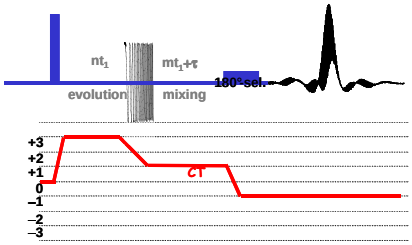


Vícekvantová NMR spektroskopie

^{27}Al MQ/MAS kyanit





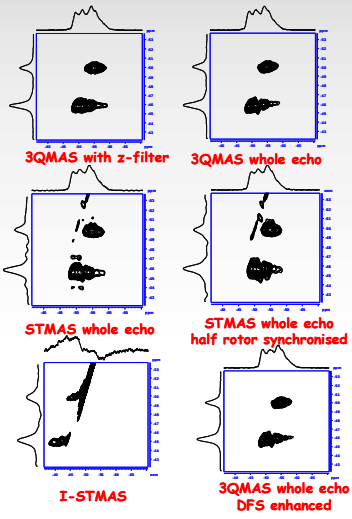


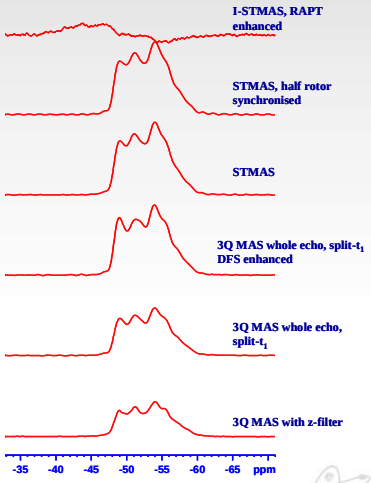
MQ
SQ ST
SQ CT

z-filter
"whole
echo"

DFS: double frequency sweep

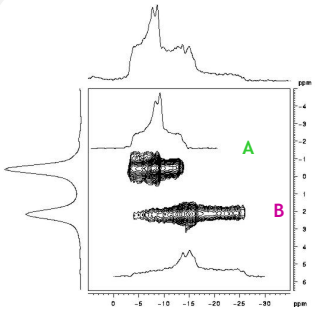
Vícekvantová NMR spektroskopie





Vícekvantová NMR spektroskopie

z-filtered 3Q MAS spectrum
of $Na_2HPO_4 * 2\ H_2O$
2.5 mm probe, 500 MHz
approx. 250 kHz RF amplitude



$$\delta_{qis} = -\frac{3(4I(I+1)-3)}{(4I(2I-1))^2} * \frac{Q_{cc}^2}{\omega_0^2}\left(1+\frac{\eta^2}{3}\right) * 10^5$$

$$\delta_{qis}^{500} = -\frac{25}{17} Q_{cc}^2 \left(1+\frac{\eta^2}{3}\right)$$

$$\delta^{3Q} = \delta_{cs} - \frac{10}{17}\delta_{qis}$$

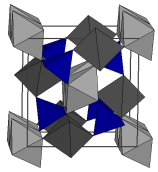
$\delta_A(F1) = -2.4 + 33/17 = -0.5$ ppm

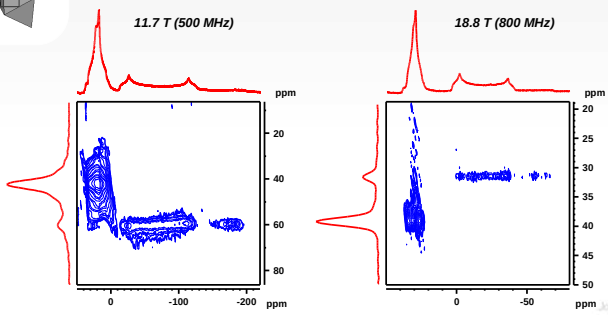
$\delta_B(F1) = -1.9 + 75/17 = +2.2$ ppm

Vícekvantová NMR spektroskopie

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

$$\delta_{3Q} = \delta_{iso} - \frac{10}{17}\delta_{qis}$$

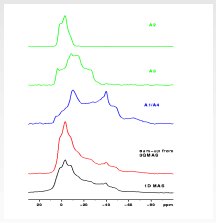


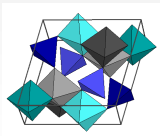


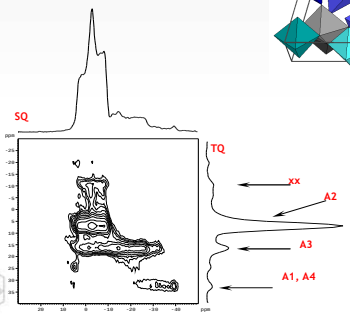
Vícekvantová NMR spektroskopie

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

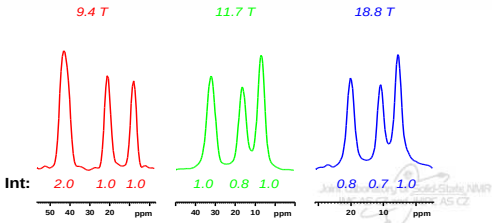
- Kyanite, z-filtered experiment at 11.7 T
- anisotropic traces
- traces for A1 and A4 cannot be resolved
- 27 kHz MAS frequency
- 250 kHz RF
- excitation pulse: 1.9 µs
- conversion pulse: 0.7 µs
- 90° selective pulse: 11 µs



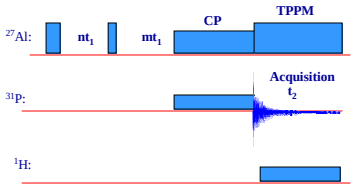


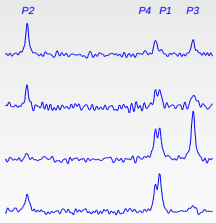


Al-27 3Q MAS traces of Kyanite at different fields



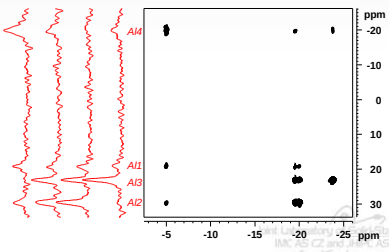
Vícekvantová korelační NMR spektroskopie



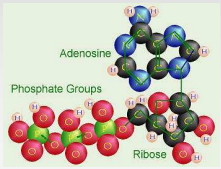


Applied RF power

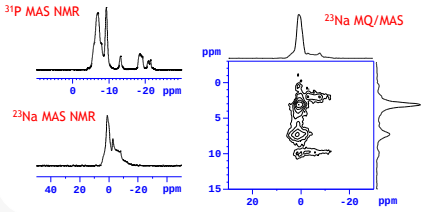
^{1}H:	decoupling:	65 kHz
^{27}Al:	3Q:	100 kHz
^{27}Al:	CP:	5 kHz
^{27}Al:	decoupling:	30 kHz
^{31}P:	CP:	42 kHz



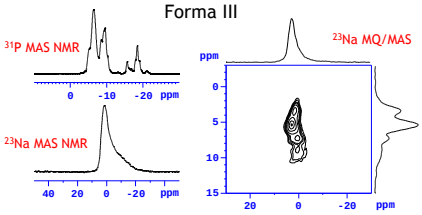
Polymorfismus ATP



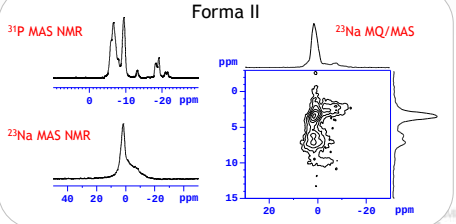
Forma I



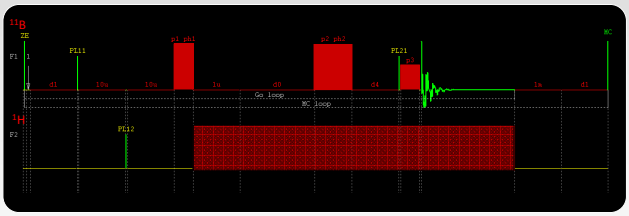
Forma III



Forma II

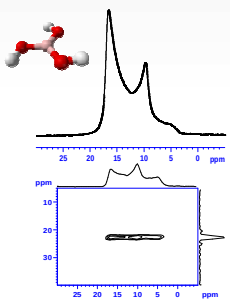


Sloučeniny boru

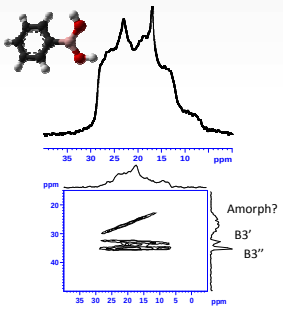


^{11}B MQ/MAS NMR

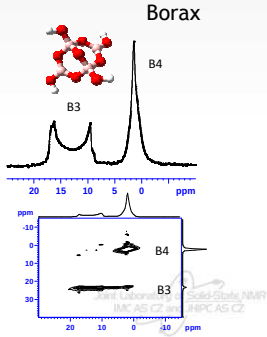
Boric acid



Phenylboronic acid

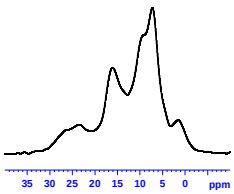


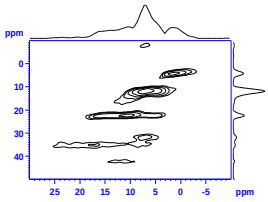
Borax

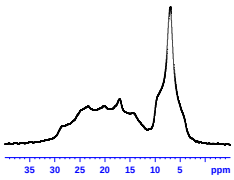


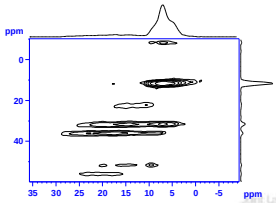
Sloučeniny boru

Deriváty kys. boronové



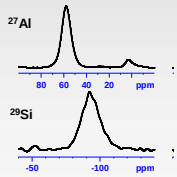




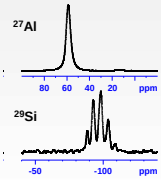


Struktura aluminosilikátových materiálů

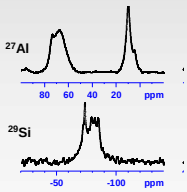
Typický Al-Si polymer



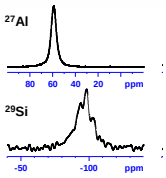
Zeolitový systém



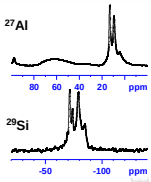
Popílek-struska-metakaolin



Alternativní geopolymery



CSH gel



Struktura aluminosilikátových polymerů

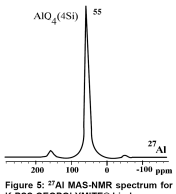


Figure 5: ^{27}Al MAS-NMR spectrum for K-PSS GEOPOLYMITE® binder

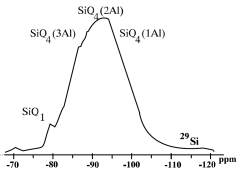


Figure 6: ^{29}Si MAS-NMR spectrum for K-PSS GEOPOLYMITE® binder

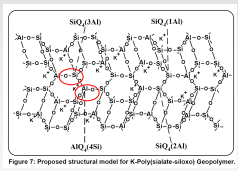


Figure 7: Proposed structural model for K-Poly(sialate-siloxo) Geopolymer.

Geopolymers and NMR, *Davidovits: Geopolymers (1994)*

^{27}Al MAS NMR

Al(VI)		15 - -5 ppm
Al(V)		38 - 25 ppm
Al(IV)	3D	50 – 68ppm
	2D	72 – 80ppm

Struktura aluminosilikátových polymerů

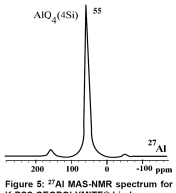


Figure 5: ^{27}Al MAS-NMR spectrum for K-PSS GEOPOLYMITE® binder

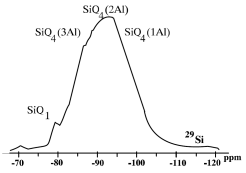


Figure 6: ^{29}Si MAS-NMR spectrum for K-PSS GEOPOLYMITE® binder

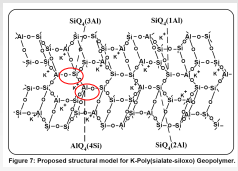
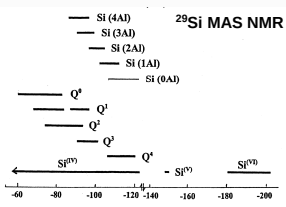


Figure 7: Proposed structural model for K-Poly(sialate-siloxo) Geopolymer.

Geopolymers and NMR, *Davidovits: Geopolymers (1994)*

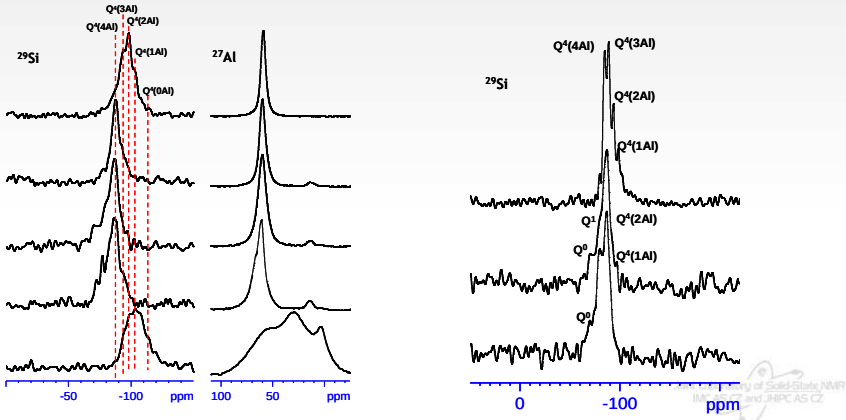
^{29}Si MAS NMR



Vznik aluminosilikátových polymerů

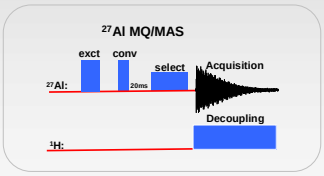
kaolinit $Al_2O_3.2SiO_2.2H_2O$

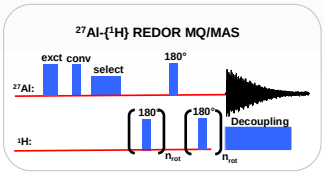
540 °C, 3h → metakaolin → metakaolin + NaOH/KOH + water glass + water → geopolymer

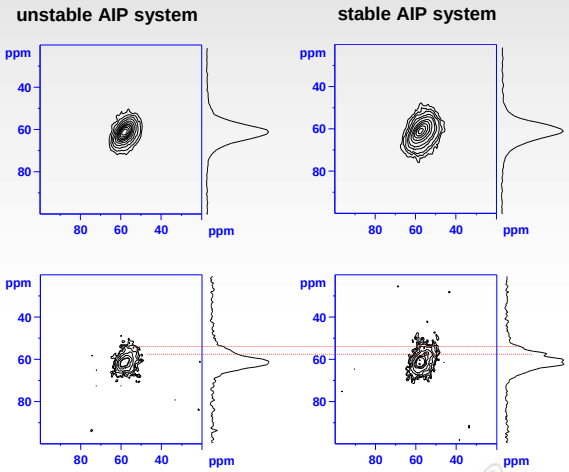


Struktura aluminosilikátových polymerů

Rozsah hydratace

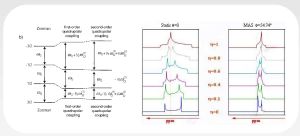




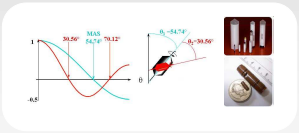


Souhrn

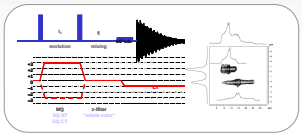
Kvadrupolová interakce



Dvojitá rotace DOR

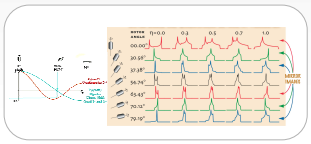


Více-kvantová spektroskopie MQ/MAS

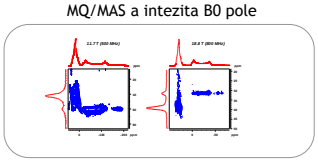


Solid-state NMR and .....

Úhel rotace a tvar spektra



MQ/MAS a intezita B0 pole



Polymorfismus org. i anorg. sloučenin